पीडीएसई / **PDSE 1025**

स्पटरिंग द्वारा विकसित मध्य से उच्च तापमान के सौर चयनात्मक लेपनों की समतल प्लेट/शून्यीकृत ट्यूब संग्राहकों की और सौर ऊष्मीय ऊर्जा उत्पादन प्रयोगों की समीक्षा

Review of sputter deposited mid- to high-temperature solar selective coatings for flat plate/evacuated tube collectors and solar thermal power generation applications

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List of abbreviations

DNI – Direct normal insolation

FPC – Flat plate collector

ETC – Evacuated tube collector

CPC – Compound parabolic concentrator

SHIP – Solar industrial process heat

IEA – International energy agency

SHC – Solar heating and cooling

CSP – Concentrated solar power

ARC – antireflection coating

ITO – Indium tin oxide

LMVF – Low metal volume fraction

HMVF – High metal volume fraction

CVD – Chemical vapor deposition

ASTM – American society of testing and materials

ATEC – Advanced thermal and environment concepts

MSTC – Materials in solar thermal collectors

UVAC – Universal vacuum collector

PTC – Parabolic trough collector

SEGS – Solar energy generating systems

HCE – Heat collector element

ASE – Archimede solar energy

ENEA – Italian national agency for new technologies, Energy and sustainable economic development

ICR – Internal circular reflector

PC – Performance criterion

IAD – Ion assisted deposition

ISO – International organization for standardization

SAF – Synthetic aromatic fluid

List of symbols

α - Absorptance

ε - Emittance

λ - Wavelength

T- Transmittance

R – Reflectance

$\Delta\alpha$ - Change in absorptance

$\Delta\varepsilon$ - Change in emittance

Abstract

Solar energy is the most abundant source of renewable energy. Solar radiation is converted into thermal energy and subsequently to electrical energy by solar thermal concentrating systems. Concentrated solar power systems use solar absorbers to convert sunlight to thermal electric power. Solar absorbers are coated with solar selective coatings with high solar absorptance and low thermal emittance. Spectrally selective coatings which are stable up to temperatures ≤ 400°C (in air and vacuum) have been developed in the past. However, in order to increase the efficiency of solar thermal power plants, solar selective coatings with high thermal stability are required. In recent years, great advances have been made in the field of solar selective coatings with high solar absorptance and low thermal emittance at higher temperatures (T > 450°C). Transition metal based solar selective coatings in particular, have emerged as novel high temperature solar selective coatings which can be used for solar thermal power plants for electricity generation. Further research is currently underway in order to increase the thermal stability of the coatings and subsequently improve the efficiency of solar thermal power plants. We present a comprehensive review of sputter deposited mid- to high-temperature solar selective coatings used for solar thermal applications. This report also describes in detail about the commercially available sputter deposited solar selective coatings for flat-plate/evacuated tube collector and solar thermal power generation applications. The worldwide scenario of parabolic trough power plants which are in operation and, under development is discussed in brief.

सौर उर्जा विपुल मात्रा में पाया जानेवाला नवीकरणीय उर्जा स्रोत है। सौर विकिरणों को पहले औष्मिक उर्जा में फिर, सौर औष्मिक संकेन्द्रिय तंत्र द्वारा, विद्युतीय उर्जा में परिवर्तित किया जाता है। संकेन्द्रित सौर उर्जा यंत्र, सौर अवशोषकों का उपयोग, सूर्य के प्रकाश को औष्मिक विद्युत उर्जा में परिवर्तित करते हैं। सौर चयनात्मक लेपन जिनमें उच्च सौर अवशोषकता और [illegible] औष्मिक एमिटेन्स होता है, उनके द्वारा सौर अवशोषकों को लेपित किया जाता है। पूर्व[illegible]ाल में स्पेक्ट्रली चयनात्मक लेपन जो तापमान ≤ 400°C (हवा और वैक्युम) तक स्थिर थे उनका विकास हो चुका है। यद्यपि, सौर औष्मिक विद्युत संयंत्रों की क्षमता को और अधिक बढ़ाने के लिए, उच्च औष्मिक स्थिरतावाले सौर चयनात्मक लेपनों की आवश्यकता है। हाल [illegible] वर्षों में, सौर चयनात्मक लेपनों के क्षेत्र में उत्कृष्ट प्रगति हुई है। इन लेपनों में (T > 450°C) [illegible] तापमान पर उच्च सौर अवशोषकता और निम्न औष्मिक एमिटेन्स पाया गया है। विशेषकर अवस्थांतर धातु आधारित सौर चयनात्मक लेपन एक नवीन उच्च तापमान सौर चयनात्मक लेपन के रूप में उभर आया है, जिनका प्रयोग सौर औष्मिक विद्युत संयंत्रों में उर्जा की उत्तपत्ति में इस्तमाल किया जा सकता है। वर्तमान में और अधिक विस्तार में अनुसंधान चल रहा है ताकि लेपनों के औष्मिक स्थिरता को बढ़या जा सके। हम यहाँ, स्पटरिंग द्वारा विकसित मध्य से उच्च तापमान के सौर चयनात्मक लेपन, जिनका सौर औष्मिक अनुप्रयोगों में इस्तमाल किया जा सकता है, उनकी एक व्यापक समीक्षा प्रसतुत कर रहे हैं। इस समीक्षा में, व्यवसायिक रूप से उपलब्ध स्पटरिंग द्वारा विकसित सौर चयनात्मक लेपन समतल प्लेट/शून्यीक्रुत ट्यूब संग्राहकों पर और सौर ऊष्मीय उर्जा उत्पादन अनुप्रयोगों की, विस्तार रूप में विवरण दी गई है। दुनियाभर के परिदृश्य में, पैराबोलिक ट्रफ विद्युत संयंत्र जो सक्रिय हैं और जो विकास के तहत हैं उन पर एक संक्षिप्त चर्चा भी यहाँ दी गई है।

1. Introduction

In recent years, renewable sources of energy have gained increased attention due to the depletion of fossil fuels, increasing concentration of green house gases and climate changes. Today, about 82% of the world's primary-energy requirements are covered by coal, natural gas, oil and uranium [1]. Approximately 12% comes from biomass and 6% from hydroelectric power. In the next 50-100 years, reduction of greenhouse gases of about 50% throughout the world is required. In order to reduce greenhouse gases, we need to use renewable energy sources, and solar energy is one of the most environmentally safe energy sources.

The simplest and most direct method of harnessing solar energy is solar thermal conversion method. Solar thermal power can only use direct sunlight called beam radiation (or) Direct Normal Insolation (DNI) i.e., the fraction of sunlight which is not deviated by clouds, fumes or dust in the atmosphere and that reaches the earth's surface in parallel beams for concentration. Suitable sites should receive at least 2000 kilowatt hours (kWh) of sunlight radiation per meter square annually; whilst best site locations should receive more than 2800 kWh/m^2/year. Among the most promising areas of the world are South-Western USA, North & South Africa, Mediterranean countries of Europe, Middle East, Iran and desert plains of India, Pakistan, Mexico, Peru, Chile and the western parts of China and Australia [2].

Solar energy is converted into thermal energy using a special kind of heat exchanger known as a solar collector. Solar collectors can be classified into two general categories: (i) non-concentrating and (ii) concentrating. In the non-concentrating type, the collector area (the area that intercepts the solar radiation) is the same as the absorber area (the area that absorbs the radiation) [3]. Flat plate collectors (FPC) and evacuated tube collectors (ETC) are non-concentrating type collectors. These collectors are mainly designed for solar hot water and industrial process heat applications which require energy delivery at temperatures in the range of 60-250°C. These collectors use both diffuse and beam solar radiation and do not require tracking of the sun. They are mechanically simpler than concentrating collectors and require less maintenance [3]. The different types of non-concentrating and concentrating type collectors are shown in Figure 1.

In the concentrating type solar collector, various types of mirrors, reflectors or concentrators are used to concentrate the solar energy and they provide higher temperatures

(i.e., 400–1000°C) than non-concentrating type collectors. Compound parabolic concentrator (CPC), central receiver or solar tower, parabolic trough collector and parabolic dish collectors are concentrating type collectors and are known as concentrated solar power (CSP) systems. The concentration ratio (i.e., ratio of the area of aperture to the area of the receiver) varies from less than unity to high values of the order of 10^5. The concentrating type collectors are classified into three types: (i) non-imaging (ii) line focusing and (iii) point focusing collectors. Non-imaging collectors have a low concentration ratio; line focusing collectors have intermediate concentration ratio and point focusing collectors have high concentration ratio. The CPC collector is a non-imaging concentrating collector. Whereas, parabolic trough and central receiver are line focusing and point focusing collectors, respectively. These CSP systems are mainly used for solar thermal power generation.

1.1. Solar thermal collectors for solar water heating applications

1.1.1 Flat plate solar water collector

The schematic diagram of a typical flat-plate solar collector is shown in Figure 2. A flat-plate collector consists of: (1) an absorber, (2) a transparent cover (3) a heat-transport fluid (water, air, etc.) (4) housing or casing and (5) insulation. The absorber consists of a solar selective coating deposited on top of a thin absorber sheet of steel or copper. A low iron solar safety glass is used as a transparent cover. Solar radiation enters the collector through the transparent cover and reaches the absorber. The absorber converts the absorbed radiation into thermal energy. In the case of a flat-plate solar water collector, good thermal conductivity is required to transfer the collected heat from the absorber sheet to the absorber pipes. The housing ensures safety and protects the absorber and insulation from the environmental impacts. Generally, rock wool or mineral wool is used as an insulation material in order to reduce the thermal losses on the back side of the absorber [3].

The efficiency of standard liquid flat-plate collectors can be improved by reducing the optical and thermal losses. This can be achieved by: (i) multiple glazing with anti-reflective glass, (ii) filling a hermetically sealed flat plate collector with a noble gas or (iii) evacuating a

hermetically sealed flat plate collector. These improved flat plate collectors can be used for solar industrial process heat (SHIP) applications [3].

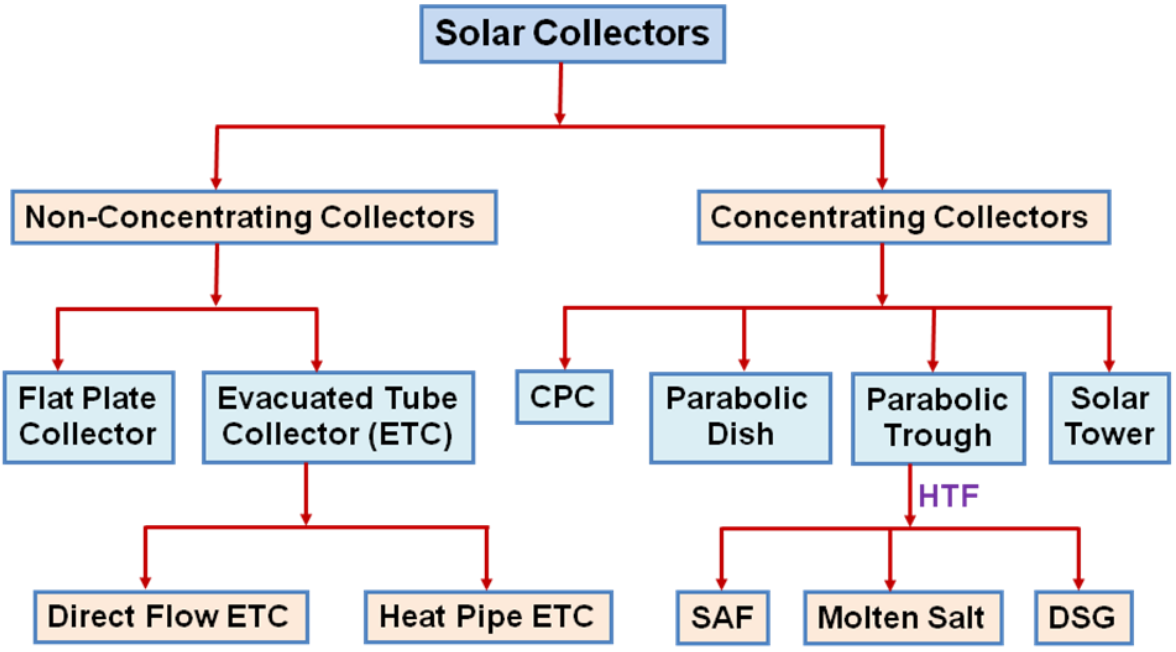

Figure 1. Types of solar collectors.

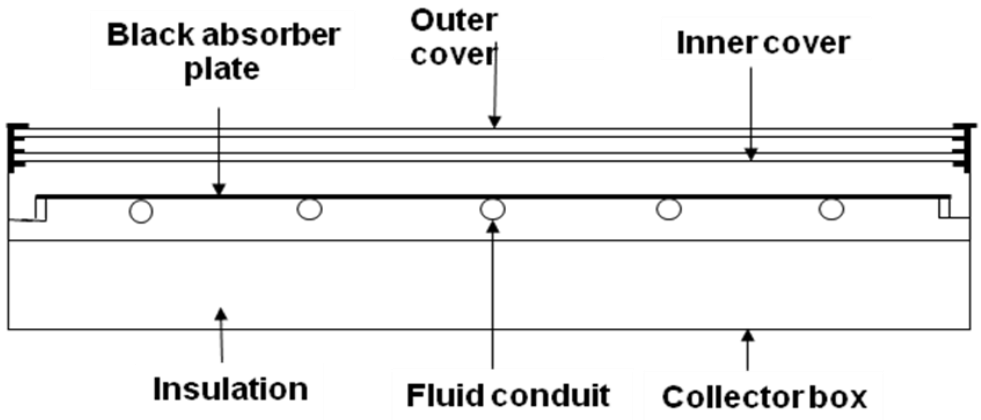

Figure 2. Schematic diagram of a flat-plate collector.

In recent years, flat plate collectors are being replaced by evacuated tube collectors since they offer certain advantages. ETCs have multiple evacuated glass tubes which heat up solar absorbers and ultimately the working fluid (water or an antifreeze – typically propylene glycol) for domestic hot water or space heating applications. The vacuum within the

evacuated tubes reduces convection and conduction heat losses, allowing them to reach considerably higher temperatures than most flat-plate collectors.

1.1.2. Evacuated tube collector

Figure 3 shows the schematic diagram of an evacuated tube collector. Each evacuated tube consists of two glass tubes made from extremely strong borosilicate glass with high chemical and thermal shock resistance. The outer tube is transparent allowing light rays to pass through with minimal reflection. The outer side of the inner tube is coated with a sputtered solar selective coating which exhibits excellent solar absorptance and low thermal emittance. The top ends of the two tubes are fused together and the air contained in the annular space between the two layers of glass is evacuated to eliminate conductive and convective heat loss. The top end of these parallel tubes is fitted to the inner storage tank.

In the process of creating vacuum, a barium getter is inserted into the base of the outer glass tube. The inner glass tube is then inserted into the outer tube with the getter centering the inner glass tube. The glass tubes are heated to a high temperature and vacuum is created. The two glass tubes are then fused together at the open end. The barium getter also serves another purpose. When the glass tubes are heated, before the ends are fused together the barium getter also becomes very hot and a pure layer of barium is coated at the bottom of the tube which will look like a chrome plate on the inside of the outer glass tube.

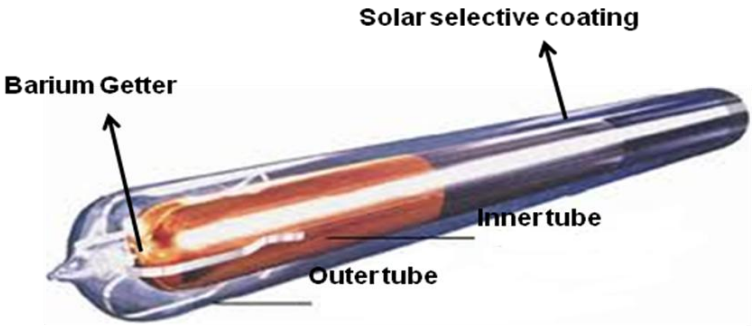

Figure 3. Schematic diagram of an evacuated tube collector.

When the glass is fractured or broken, the shiny chrome changes to a milky color, thus, making it easy to identify the vacuum loss in the particular glass tube. The advantage of an evacuated tube collector when compared to a flat-plate collector is that the constant profile of the round evacuated tubes is always perpendicular to the sun's rays. Therefore the energy absorbed is approximately constant over the course of a day. Evacuated tube collectors can be classified in two main groups: (i) direct flow evacuated tube collectors and (ii) heat pipe evacuated tube collectors.

1.1.3. Direct flow evacuated tube collector

In this type of collector, the whole interior of a glass tube is evacuated. The flat or curved absorber as well as fluid inlet and fluid outlet pipes are placed inside the evacuated tube. The absorber is coated with a spectrally selective coating. Single evacuated tubes often have diameters between 70 and 100 mm [3]. Direct flow evacuated tube collector has different configurations such as separate tubes for fluid inlet and outlet (Figure 4(a)), concentric inlet and outlet pipes (Figure 4(b)), lenz tube (i.e., concentric pipe configuration in which the fluid inlet is copper and the outlet is glass) and Sydney tube (two glass tubes fused together and the space in between is evacuated).

1.1.4. Heat pipe evacuated tube collector

Figure 5 shows the schematic diagram of a heat-pipe evacuated tube collector. The heat pipe is hollow with low pressure inside. A heat pipe evacuated tube collector uses alcohol or water with some special additives in vacuum to absorb solar energy. Due to the vacuum, the alcohol or water will evaporate at a low temperature of 25°C to form vapor. This vapor rises up the collector tube to the heat exchanger where heat transfer to the solar fluid takes place. Subsequently, the vapor condenses back to liquid and flows back down the collector tube. Therefore, heat pipe evacuated tubes are installed with a tilt of at least 25°. There are two types of heat pipe evacuated tube collector: (i) heat exchanger extends directly into the manifold (wet connection) and (ii) heat exchanger connected to the manifold by a heat-conducting material (dry connection). In a dry connection collector, the condenser completely surrounds the collector tube. This provides good heat transfer between the tube and the heat exchanger and allows tubes to be replaced without the need to drain the solar fluid. In a wet connection collector, the tube is submerged in the heat transfer fluid. Therefore, if a tube needs to be replaced then the system must be drained. The major difference between the heat pipe and direct flow evacuated tube collector is that, in heat pipe ETC, the heat transfer fluid is not directly connected to the solar loop.

1.2. Solar thermal collectors for solar industrial process heat applications

Industrial process heat is one of the least developed solar thermal applications so far. Even though the potential for SHIP applications is huge, it is difficult to standardize solar thermal systems for a wide variety of industrial applications. Solar industrial process heat applications often require temperatures in the range of 80-250°C. Medium temperature collectors are suitable for SHIP applications, but only a few are available in the market today.

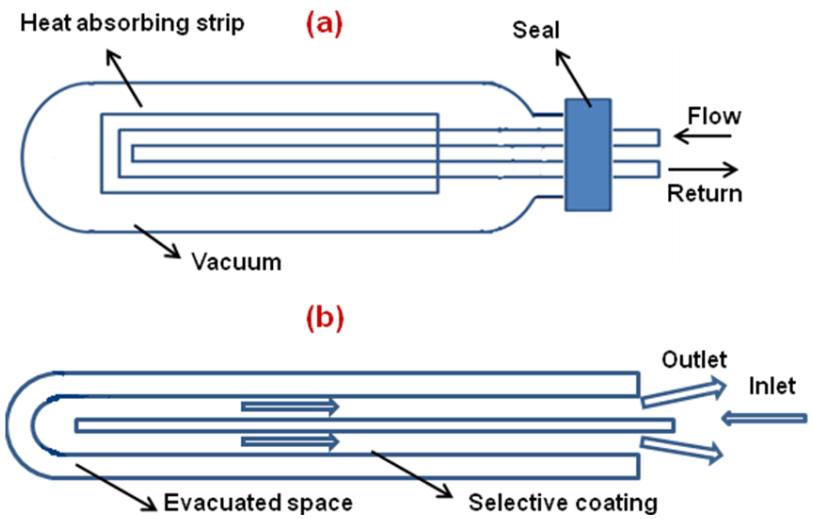

Figure 4. Different configurations of an evacuated tube collector: (a) separate inlet and outlet pipes and (b) concentric inlet and outlet pipes.

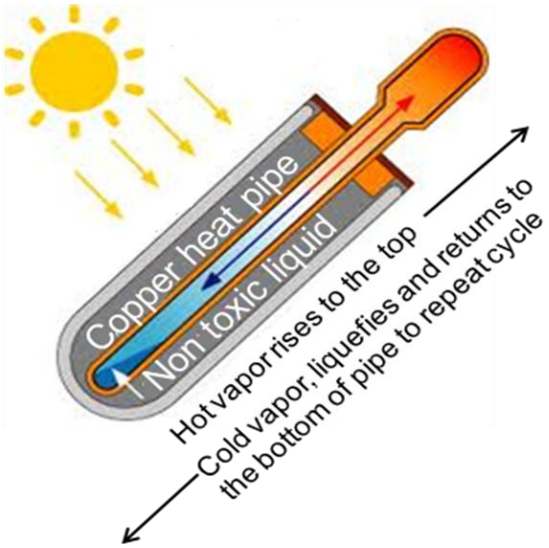

Figure 5. Schematic diagram of a heat-pipe evacuated tube collector.

Therefore, the International Energy Agency's Solar Heating and Cooling Programme (IEA-SHC) developed and tested three categories of medium temperature collectors as part of their Task 33: (i) improved flat plate collectors (discussed above), (ii) concentrating flat plate and evacuated tube collectors and (iii) other-more highly-concentrating collectors (i.e., compound parabolic concentrator (CPC)). The details of these collectors are explained elsewhere [4]. The Task 33 Report also mentioned that currently about 90 operating solar thermal plants for process heat are reported worldwide, with a total capacity of about 25 MW (35000 m^2), the

details of which have been described elsewhere [4]. At the end of 2008, the installed solar thermal capacity worldwide was about 151.7 GW (217 million m^2). Of this, 131.8 GW were accounted for flat and evacuated tube collectors, 18.9 GW for unglazed plastic collectors and 1.2 GW for air collectors [5].

1.2.1. Compound parabolic concentrator

CPC collector (Figure 6) uses a compound parabolic concentrator (non-imaging type) to concentrate solar radiation on an absorber. CPC collectors admit a greater amount of light and needs less accurate tracking when compared to parabolic trough collector (PTC). Therefore, they bridge the gap between the low temperature flat-plate collectors ($T < 80°C$) and the high temperature focusing concentrators ($T > 400°C$).

For solar thermal power generation, it is desirable to deliver energy at temperatures higher than those of evacuated tube (non-concentrated) and CPC collectors. A concentrating type collector can be used for high temperature applications such as to produce steam for thermal power generation. Solar thermal power systems also known as concentrating solar power systems use concentrated solar radiation as a high temperature energy source to produce electricity using thermal route. Direct solar radiation can be concentrated and collected by a range of CSP technologies to provide medium to high temperature heat. The CSP systems are shown in Figure 7.

1.3 Central receiver (or) solar tower

A circular array of heliostats (large individually tracking mirrors) is used to concentrate sunlight on to a central receiver mounted on the top of a tower. A heat-transfer medium in the central receiver absorbs the highly concentrated radiation reflected by the heliostats and converts it into thermal energy which is subsequently used for the generation of superheated steam for turbine operation.

1.4 Parabolic dish collector

A parabolic dish shaped reflector is used to concentrate sunlight on to a receiver located at the focal point of the dish. The concentrated beam radiation is absorbed into the receiver to heat a fluid or gas (air) to approximately 750°C. This fluid or gas is then used to generate electricity through a small piston or Stirling engine or a micro turbine, attached to the receiver.

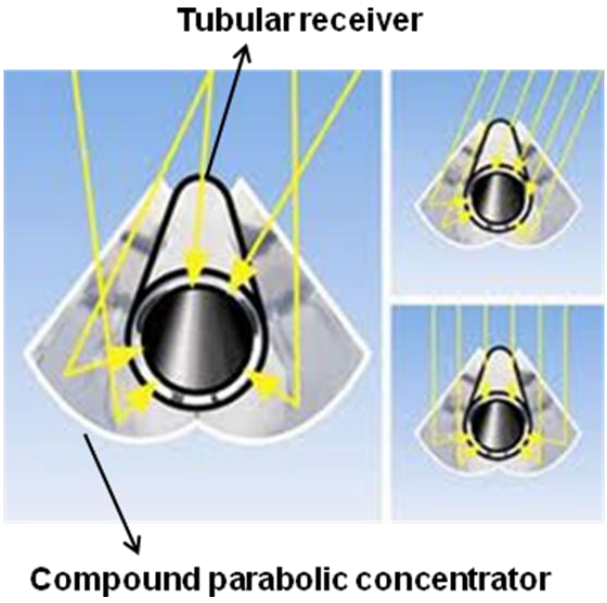

Figure 6. Schematic diagram of a compound parabolic concentrator collector.

Figure 7. Types of concentrated solar power systems.

1.5 Parabolic trough collector

Parabolic trough systems use trough-shaped mirror reflectors to concentrate sunlight on to the receiver tubes through which a thermal transfer fluid is heated to roughly 400°C and then used to produce superheated steam. The heat is then used to operate a conventional power cycle, for example, through a steam turbine or a Stirling engine.

1.6 Parabolic trough collector - Components and advantages

The primary components of a trough system are:

(i) Parabolic trough concentrator: The parabolic trough concentrator reflects direct solar radiation onto a receiver located at the parabola's focal point. The reflective surface, often

silver or aluminum films is deposited on some type of rigid support. Currently, the most commonly used support structures are metallic, glass or plastic tubes.

(ii) Absorber tube: The absorber tube is one of the most important components of a trough system. The absorber tube is made of two concentric tubes that lie along the parabolic trough's focal point. The outer tube (made of glass) is separated from the inner tube (made of metal) by a vacuum layer. This reduces heat loss and increases the overall efficiency. A working fluid is circulated through the inner tube and absorbs solar radiation energy as heat.

(iii) Working fluid: The working fluid varies depending on the trough technology. For lower temperature applications (less than 200°C), demineralized water with an ethylene-glycol mixture is used as the working fluid. For higher temperatures, (200 - 450°C) synthetic aromatic oil is often used as the working fluid. Direct steam generation (DSG) in parabolic trough collectors eliminates the use of heat exchangers and expensive heat transfer fluids. Therefore, it is a promising option to improve the efficiency and reduce the operating costs of parabolic trough power plants. Newer technologies use molten salts as the working fluid.

(iv) Solar tracking system: A parabolic trough power plant's solar field consists of a large, modular array of single-axis tracking parabolic trough solar collectors. Many parallel rows of these solar collectors span across the solar field, usually aligned on a north-south horizontal axis.

(v) Support structure: The entire parabolic trough system is supported by a rigid metallic support structure. The structure supports the mirrors and receivers and maintains their optical alignment. It allows the collector to rotate, so that the mirrors and receivers can track the sun. Generally, the support structures are made from galvanized steel or extruded aluminum.

Improving the properties of the solar selective coating on the receiver and increasing the solar field operating temperature above 400°C can improve the efficiency of a parabolic trough solar power plant and reduce the cost of solar electricity. In order to achieve this, new efficient spectrally selective coatings are needed which have high absorptance (α) in the wavelength range of 0.3-2.5 μm and low emittance (ε) in the infrared region, at higher operating temperatures (both in air and vacuum).

1.7 Types of spectrally selective coatings

Spectrally selective coatings used on the receiver tubes can be categorized into six types and are shown schematically in Figure 8: (i) intrinsic absorber (ii) absorber-reflector

tandem (iii) multilayer absorber (iv) metal-dielectric composite (i.e., cermet) (v) textured surface and (vi) selectively solar-transmitting coating on a black body absorber [6].

1.7.1 Intrinsic absorber

An intrinsic solar absorber is made of a single material that is wavelength selective. There are no naturally occurring materials exhibit intrinsically ideal solar selective properties, but some materials have moderate selective properties. The ideal characteristic of a spectrally selective absorber is shown in Figure 9. Various transition metals and semiconductors show such selective characteristics, but both need to be greatly modified to serve as intrinsic absorbers. Some examples are HfC, MoO_3 doped Mo, ReO_3, etc. [6,7]. The main disadvantage of an intrinsic absorber is that the cross over from low to high reflectance occurs at too short wavelengths.

1.7.2 Tandem absorber

A tandem absorber consists of at least two materials/layers with different optical properties. Each material/layer has its own optical property and together they make an absorber with solar selective properties. There are two types of tandem absorbers namely: (i) absorber-reflector tandem (i.e., dark mirror) and (ii) heat mirror.

1.7.2.1 Absorber-reflector tandem

A coating transparent in the infrared region and having high solar absorptance in the solar wavelength range, deposited on top of a highly infrared reflecting substrate constitutes an absorber-reflector tandem. Thus the tandem absorber has high solar absorptance due to the absorbing layer and low thermal emittance due to the metallic reflector substrate. An anti-reflection coating (ARC) can be deposited on top of the absorbing layer to reduce front surface reflections.

1.7.2.2 Heat-mirror

In the heat mirror configuration, a selectively reflecting material is deposited on top of an absorbing substrate. The top layer reflects the infrared radiation and allows the visible radiation, while the bottom layer absorbs the visible radiation. This system thus works in reverse to that of the regular tandem absorber. The schematic diagram of a heat-mirror configuration is shown in Figure 10. Typical example of a heat mirror is indium tin oxide (ITO) on silicon. ITO film sprayed directly onto a silicon absorber serves as an antireflection coating for the silicon in the visible region and as an emittance suppressor in the infrared region [8].

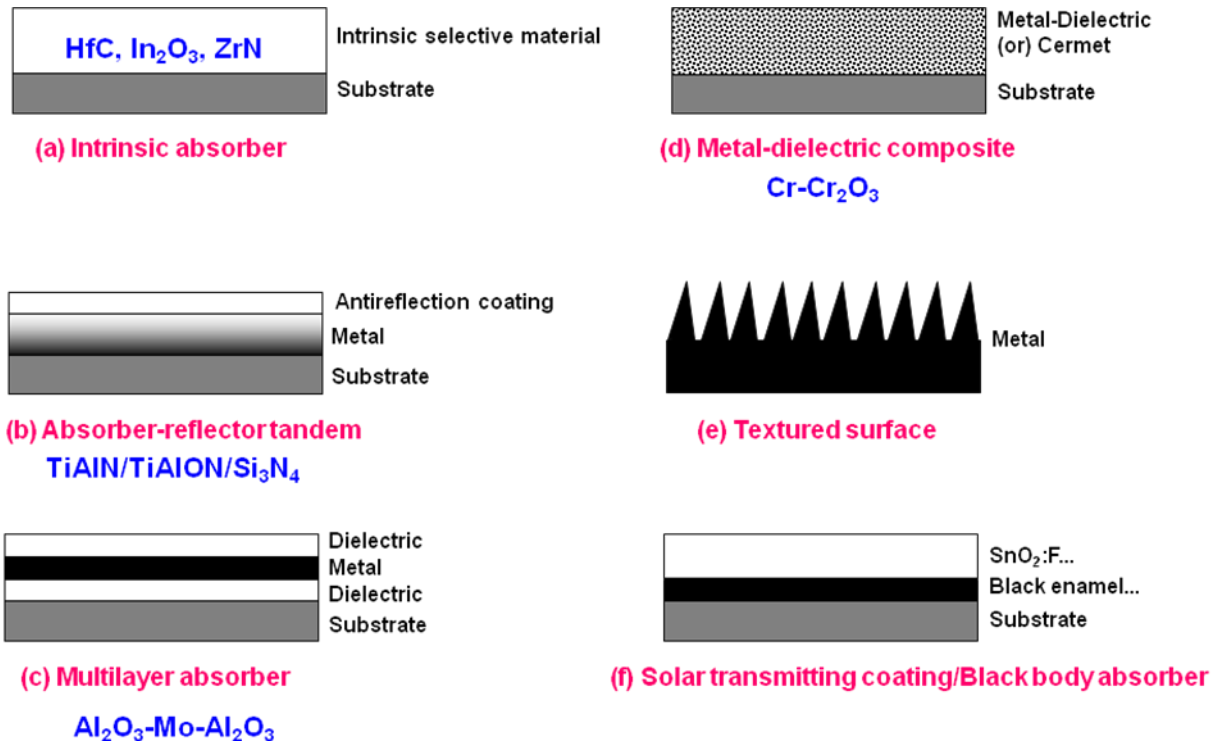

Figure 8. Types of solar selective coatings.

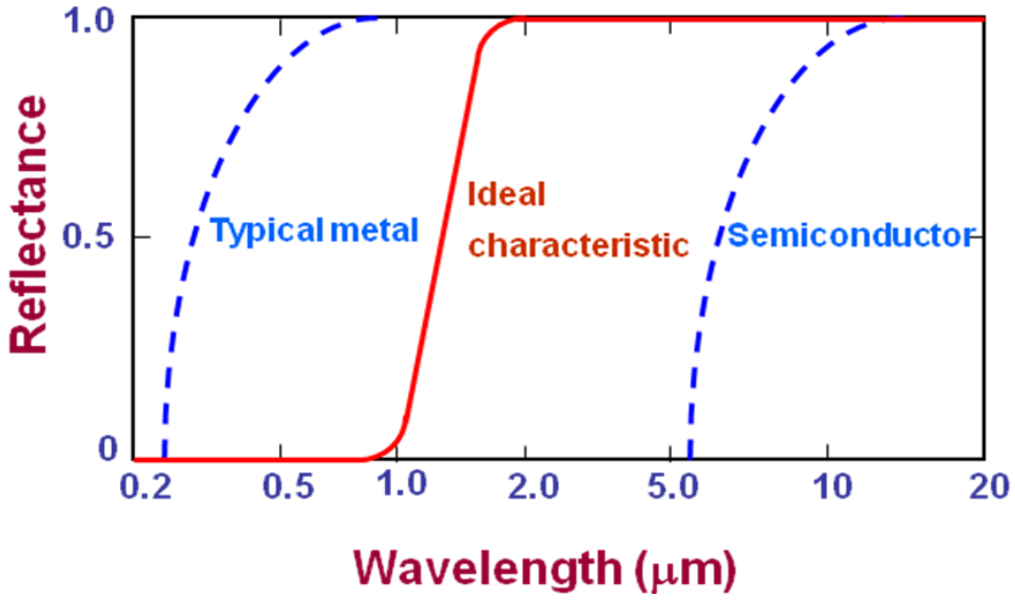

Figure 9. Ideal characteristics of a spectrally selective absorber.

Figure 10. Schematic diagram of a heat mirror.

1.7.3 Multilayer absorber

A multilayer absorber is composed of several alternate layers of dielectric and semitransparent metallic materials. The multilayer absorber should be deposited on a sufficiently polished metal substrate or a substrate covered by an opaque metal layer with high reflectivity in the infrared region which gradually drops in the visible region. A thin semitransparent metallic layer is sandwiched between two dielectric layers. The top dielectric layer reduces the visible reflectance and broadens the wavelength region of high absorption. Various multilayer absorbers using different metals (e.g., Mo, Cu, Al, Hf, Ni) and dielectric layers (e.g., Al_2O_3, HfO_2, SiO_2, ZnS) have been cited in the literature for high-temperature applications [9].

1.7.4 Metal-dielectric composite coating

Metal-dielectric composites or cermets consist of fine metal particles embedded in a dielectric matrix or a porous oxide impregnated with metal. These coatings are transparent in the IR region and are absorbing in the visible region due to interband transitions in the metal and small particle resonance. The metal-dielectric concept offers a high degree of flexibility, and the solar selectivity can be optimized by a proper choice of constituents, coating thickness, particle concentration, size, shape and orientation. Ungraded single cermet layers with an isotropic metal volume fraction, deposited on a copper reflector and topped by an antireflection layer show an absorptance of about 0.80. Pekhrun et al. have reported an absorptance of 0.85 and emittance of 0.027 for Cr-SiO single layer cermets [10]. In order to achieve absorptance greater than 0.90, a double-layer cermet structure model has been developed. The double layer cermet structure has higher photo-thermal conversion efficiency than single layer cermet or graded cermet structure. A typical double-layer cermet structure

from the substrate to the surface consists of: (i) an AR layer, (ii) an absorbing layer composed of two homogenous cermet layers, i.e., a low metal-volume fraction (LMVF) cermet layer on a high metal volume fraction (HMVF) cermet layer; and (iii) a metallic infrared reflector layer to reduce substrate emittance [11]. The schematic diagram of a double layer cermet coating is shown in Figure 11.

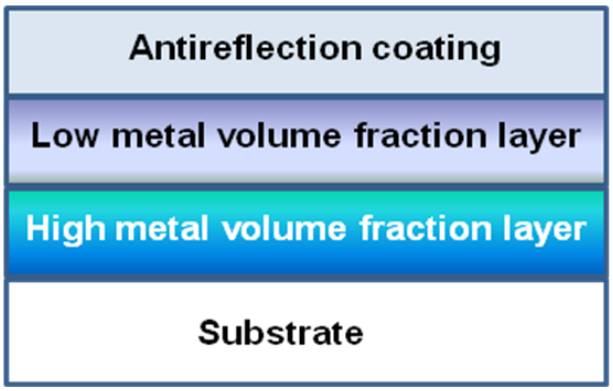

Figure 11. Schematic diagram of a double layer cermet coating.

1.7.5 Surface texturing

Surface texturing is a common technique to obtain spectral selectivity by the optical trapping of solar energy. Textured surfaces can produce high solar absorptance by multiple reflections among needle-like, dendritic or porous microstructure [12,13]. The emittance can be adjusted by modifying the microstructure of the coatings with ion-beam treatments.

1.7.6 Selectively solar-transmitting coating on a black body absorber

A selectively solar–transmitting coating on a black body absorber consists of a highly doped semiconductor (e.g., SnO_2:F, SnO_2:Sb, In_2O_3:Sn and ZnO:Al) over an absorber with a proven long term durability [14].

1.8 High temperature solar selective coating

For CSP applications, the spectrally selective coatings should have high thermal stability (T > 400°C) in air and vacuum. Coatings which are thermally stable above 400°C are called high-temperature solar selective coatings and coatings stable in the range of 100-400°C are called mid-temperature solar selective coatings. The requirements of a high temperature solar selective coating are:

- High solar absorptance ($\alpha > 0.90$)
- Low thermal emittance ($\varepsilon < 0.10$)
- Long term stability at desired operating temperatures and environmental conditions

- Stability at high temperatures during collector stagnation
- Durability for the life of the collector
- Applicability to given substrate materials
- Reproducibility
- Reasonable cost

Spectrally selective coatings for solar thermal applications can be prepared using various methods such as electroplating, chemical vapor deposition (CVD), vacuum evaporation, sputtering, anodization, chemical conversion, solution growth and spray pyrolysis. Among these, magnetron sputtering technology has been widely used for large-area deposition. Magnetron sputtering process is a dry, clean and eco-friendly technique for depositing a variety of coatings. High melting point nitrides (including transition metal nitrides) with controlled microstructure, which are chemically inert and very hard, can be deposited by sputtering. Furthermore, improved optical properties can be achieved for solar selective coatings deposited using sputtering technique. A worldwide survey of industrial sputtering system manufacturers are given in Appendix A.

2. Characterization of selective surfaces

This section deals with characterization and testing of spectrally selective coatings. The service lifetime estimation of mid-temperature solar selective coatings according to International Energy Agency Solar Heating and Cooling Program (IEA SHC) Task X is also presented in this section. The performance of a solar selective coating is evaluated from its solar absorptance and thermal emittance. Generally, when radiation falls on a surface, it may be partially reflected, transmitted or absorbed. According to Kirchoff's law, at equilibrium, for a given wavelength (λ) and temperature (T), the emittance (ε) of any body is equal to its absorptance (α):

$$\varepsilon(\lambda,T) = \alpha(\lambda,T) = 1 - R(\lambda,T) - T(\lambda,T) \quad (1)$$

where, R is the reflectance and T is the transmittance.

If the coating is opaque, the transmittance, $T(\lambda,T)$ is equal to zero and Eq. (1) becomes:

$$\varepsilon(\lambda,T) = \alpha(\lambda,T) = 1 - R(\lambda,T) \quad (2)$$

2.1. Emittance and absorptance measurements

In general, emittance measurements are difficult and tedious because emittance is an extrinsic property of a material, i.e., it is a function of several variables. Although many methods have been proposed and developed for measuring emittance, a standard procedure or a universally accepted methodology does not exist yet. Qualitatively, the emissivity can be estimated by four basic methods: (i) optical reflectivity method, (ii) radiation thermometry, (iii) calorimetric method and (iv) portable ambient (differential thermopile) emissometer.

2.1.1. Reflectivity method

Reflectivity method involves illuminating a sample with infrared energy and measuring the percentage of energy reflected from the surface of the sample. The thermal emittance can be calculated from the reflectance spectrum, which is defined as [15]:

$$\varepsilon = \sum_{j=1}^{n}(1-R_j)\Delta f_j = 1 - \sum_{j=1}^{n} R_j \Delta f_j \quad (3)$$

where Δf_j is the energy increment in the blackbody spectrum which can be determined from Table 1 as the difference in $f_{0\text{-}\lambda T}$ at the wavelengths defining the segment. If the energy increments are equal,

$$\varepsilon = \frac{1}{n}\sum_{j=1}^{n}\varepsilon_j = 1 - \frac{1}{n}\sum_{j=1}^{n} R_j \quad (4)$$

Table 1. Fraction of blackbody radiation energy between zero and λT for even fractional increments.*

$f_{0-\lambda T}$	λT (μm K)	λT at Midpoint	$f_{0-\lambda T}$	λT (μm K)	λT at Midpoint
0.05	1880	1660	0.55	4410	4250
0.10	2200	2050	0.60	4740	4570
0.15	2450	2320	0.65	5130	4930
0.20	2680	2560	0.70	5590	5350
0.25	2900	2790	0.75	6150	5850
0.30	3120	3010	0.80	6860	6480
0.35	3350	3230	0.85	7850	7310
0.40	3580	3460	0.90	9380	8510
0.45	3830	3710	0.95	12500	10600
0.50	4110	3970	1.00	∞	16300

*From "Solar Engineering of Thermal Processes" by John A. Duffie and William A. Beckman, Third edition, John Wiley & Sons, Inc., p. 144.

While calculating emittance from the spectral data taken at room temperature, it is assumed that the spectral characteristics do not change with increasing temperature. This is valid only if the material is invariant and does not undergo a phase change, breakdown or oxidation at higher temperatures [9].

The calculation of absorptance is similar, except that the incident radiation must be specified instead of blackbody radiation (i.e., incident energy spectrum is used for absorptance calculations). Table 2 provides the information for calculation of absorptance for terrestrial applications [15]. The incident radiation is divided into increments, and the contributions of these increments are summed to obtain α for that incident radiation. If Δf_j, is the increment in incident radiation, the contribution to α is $\alpha_j \Delta f_j$. Summing up,

$$\alpha = \sum_{j=1}^{n} \alpha_j \Delta f_j = \sum_{j=1}^{n} (1 - R_j) \Delta f_j = 1 - \sum_{j=1}^{n} R_j \Delta f_j \tag{5}$$

and if the energy increments Δf_j are equal,

$$\alpha = \frac{1}{n} \sum_{j=1}^{n} \alpha_j = \frac{1}{n} \sum_{j=1}^{n} (1 - R_j) = 1 - \frac{1}{n} \sum_{j=1}^{n} R_j \tag{6}$$

Table 2. Spectral distribution of terrestrial beam normal radiation at air mass 1.5, precipitable water 1.42 cm, O_3 = 0.34 atm-cm, CO_2 = 370 ppm, in equal increments of energy.*

Energy Band ($f_i - f_{i+1}$)**	Wavelength Range (μm)	Mid-point Wavelength (μm)
0.0-0.05	0.280-0.426	0.396
0.05-0.10	0.426-0.470	0.451
0.10-0.15	0.470-0.508	0.490
0.15-0.20	0.508-0.545	0.527
0.20-0.25	0.545-0.581	0.563
0.25-0.30	0.581-0.617	0.599
0.30-0.35	0.617-0.653	0.635
0.35-0.40	0.653-0.691	0.672
0.40-0.45	0.691-0.732	0.710
0.45-0.50	0.732-0.777	0.752
0.50-0.55	0.777-0.822	0.798
0.55-0.60	0.822-0.871	0.846
0.60-0.65	0.871-0.929	0.896
0.65-0.70	0.929-1.012	0.981
0.70-0.75	1.012-1.080	1.044
0.75-0.80	1.080-1.201	1.142
0.80-0.85	1.201-1.300	1.249
0.85-0.90	1.300-1.588	1.510
0.90-0.95	1.588-1.974	1.678
0.95-1.00	1.974-5.000	2.232

*From "Solar Engineering of Thermal Processes" by John A. Duffie and William A. Beckman, Third edition, John Wiley & Sons, Inc., p. 64.
**spectral distribution curve

2.1.2. Radiation thermometry

Radiation thermometry is a convenient non-contact temperature measurement technique. In this method, the surface temperature is extrapolated from the intensity of thermal radiation emitted from the surface, which is referenced to an ideal surface (i.e. blackbody) at the same temperature. Three types of radiation thermometry are used to determine the surface temperature: (i) spectral, (ii) dual-wavelength and (iii) multi-spectral radiation thermometry. Spectral radiation thermometry relies upon intensity measurement at

one wavelength and a constant emissivity value to extrapolate the surface temperature. Dual wavelength radiation thermometry employs intensity measurements at two wavelengths and an emissivity compensation algorithm to determine the surface temperature. Multispectral radiation thermometry utilizes intensity measurements at three or more wavelengths and an emissivity model to obtain the surface temperature. The details of radiation thermometry method have been explained elsewhere [16].

2.1.3. Calorimetric method

Calorimetric methods for determining emittance or absorptance involve the measurement of radiation gain or loss from an absorbing and/or emitting surface. Two basic techniques are used. The steady state technique involves the measurement of the amount of energy required to keep a sample at a specific temperature above its environment. The transient technique measures the rate of temperature change of a sample being heated or being allowed to cool. The details of the different techniques have been described elsewhere [17,18].

2.1.4. Portable ambient emissometer

In 1976, Committee C-16 on Thermal Insulation of the American Society For Testing and Materials (ASTM) published a standard test method (ASTM C 835 – 06) to measure the total hemispherical emittance of surfaces up to 1400°C by calorimetric test method [19]. In 1997, the committee published another standard test method (ASTM C1371-04a) to measure the emittance at near room temperature using a portable differential thermopile emissometer [20]. The portable instrument used for the standard test method was model AE emissometer of M/s. Devices & Services Co. As per the request of Committee C-16 of ASTM, the Oak Ridge National Laboratory, USA coordinated a round-robin study to evaluate the Devices &Services model AE emissometer, the results of which have been described elsewhere [21].

The emissometer (model AE) is a special purpose instrument to measure the emittance of absorber coatings used for flat plate solar thermal collectors, wherein the maximum working temperature of the collector is of the order of 80-85°C. The emissometer is heated to 82°C, so that the sample to be measured need not be heated. At 82°C, the spectral range of the thermal radiation emitted from the surface is in the range of 3-30 μm. The detector used in the emissometer consists of a differential thermopile with low and high emittance areas, which ensures near constant response to the emitted radiation in this

wavelength range. The instrument is calibrated using standard samples and the emissometer has a repeatability of ± 0.01 units [21].

Absorptance can also be measured using solar spectrum reflectometer (Model SSR) of M/s. Devices and Services. For the solar spectrum reflectometer, the source of the illumination is a tungsten-halogen lamp. The radiation reflected by the sample is measured at an angle of 20º from the normal, with four filtered detectors (UV, blue, red and infrared). A solar spectrum measurement is achieved by adding up the four outputs in the appropriated proportions. Air mass 2 is used to calibrate the solar reflectometer.

Recently, Saeed Moghaddam et al. have used a commercially available thermopile heat flux sensor (Advanced Thermal and Environmental Concepts (ATEC Inc.)) to measure the total hemispherical emissivity, the details of which have been described elsewhere [22]. The emissivity is calculated by directly measuring the heat flux passing through the surface using a heat flux gauge. Unlike storage-based calorimetric methods, this method does not require application of known amounts of heat to the surface or the temperature history of a known amount of thermal mass to calculate the surface emissivity. Application and operation of this method is much simpler than calorimetric methods because it does not require careful thermal insulation of the substrate from the surroundings.

Various types of calorimeters/emissometers have been developed to measure the spectral/hemispherical emittance of a surface [17,18,21,23-30]. Beens et al. designed and developed a calorimetric emissometer to determine the hemispherical emittance [25]. In 1980, Willrath and Smith developed a new transient temperature emissometer to measure the total hemispherical emittance [24]. This emissometer is a modified version of an earlier instrument (i.e. calorimeter), which was developed by Willrath and Gammon in 1978 [31]. Vader et al. have designed and developed a high temperature emissometer for porous and particulate dielectrics [28]. Recently, Advanced Fuel Research, Inc. developed an automated FTIR based bench-top high temperature emissometer (50-2000°C), which measures spectral emissivity over a broad spectral range from the near to mid IR (0.8-20μm) region and also determines the surface temperature at the measurement location [26,32]. But, to the best of our knowledge, only a few emissometers are commercially available in the market and are listed in Table 3.

Table 3. List of commercially available emissometers

Company	Model No.	Wavelength range (μm)	Temperature (°C)
International Technology Corporation, USA#	McDonald Emissometer 2145	0.3-2	100
Surface Optics, USA	ET100	3-30	Ambient
AZ Technology, USA	TEMP 2000A	3-35	Ambient
Devices and Services, USA	AE	3-30	80
Advance Fuel Research, USA*	205 NB and 205 WB	0.8-20	50-2000
Advanced Thermal and Electric Concepts, Inc., USA	HFBE	3-30	-60 to 80
Lion Research Corporation, USA	25B	3-30	Ambient

#Currently not available in market
*Currently not being built for sale

2.2. Performance criterion evaluation

In addition to high solar absorptance and low thermal emittance, long term thermal stability is also very important for spectrally selective coatings used in the flat plate/evacuated tube collectors. A procedure for accelerated life testing of solar absorber surfaces was developed within the framework of the working group MSTC (Materials in Solar Thermal Collectors) of the IEA-SHCP. The procedure was formulated as a standard and submitted to ISO (International Organization for Standardization) at the beginning of 1997 as a 'Draft Proposal'. It carries the designation ISO/CD 12592,2 '*Solar Energy – Materials for flat-plate collectors – Qualification test procedures for solar surface durability*'. The proposed standard describes in detail, the procedure for the examination of the long-term stability of solar absorber coatings used in flat-plate collectors for domestic hot water systems. Possible degradation caused by the thermal load, condensation, high humidity and air pollutants (sulphur dioxide) have been taken in to account while formulating the procedure. For estimating the acceptable service life time of an absorber coating, the IEA-SHC Task X [33-35] has defined a performance criterion function (PC) for flat plate collector selective absorber testing. The PC describes the influence in the change of solar absorptance ($\Delta\alpha$) and emittance on the solar fraction:

$$PC = -\Delta\alpha + 0.25\Delta\varepsilon \leq 0.05, \quad (8)$$

An absorber surface is qualified if it fulfills the performance criterion for a service lifetime of at least 25 years. Several papers have been published describing the procedure for

thermal stability tests according to the IEA SHC recommendations [33-37]. The thermal stability test consists of an initial test at 250°C for 200 h followed by an adhesion test. The sample is qualified without further tests if the PC is ≤0.015 and surface adhesion is 0.15 MPa after the initial test. Otherwise, additional tests are required at different temperatures, which are shown in the appendix B. No similar criterion has been developed for testing the service lifetime of high temperature absorbers for CSP applications.

3. Mid-temperature solar selective coatings

In 1976, G.L. Harding from University of Sydney developed various transition metal carbide and silicide coatings for solar thermal applications. The metal silicides and carbides of chromium, iron, molybdenum, stainless steel, tantalum, titanium, tungsten were deposited by reactive sputtering on bulk and sputtered copper substrates [38-40]. A solar absorptance of 0.76-0.80 and a thermal emittance of 0.02-0.03 were observed at room temperature for the homogeneous metal carbides prepared on bulk copper. Sputtered Mo/MoC on bulk Cu exhibited the highest optical properties (α = 0.90 and ε = 0.035). The coatings deposited on bulk and sputtered copper substrates exhibit different aging effects. No deterioration was observed after 250 h at 250°C and 400°C (120 h) in air for the films on bulk copper, whereas the coatings deposited on sputtered copper began to deteriorate slightly at 250°C.

Similarly, the homogenous metal silicides on bulk copper have α = 0.75-0.81 and ε = 0.02-0.03 at room temperature. These coatings were thermally stable at 400°C in vacuum. When deposited on sputtered copper, the absorptance increased to 0.81-0.86 because sputtered copper coatings have lower reflectance than the bulk copper substrates. Among these, stainless silicide exhibited high absorptance of 0.87 and low thermal emittance of 0.045 on evaporated Ni. The multilayer metal silicide coatings deposited on Cu substrates exhibited higher absorptance in the range of 0.89-0.93 and emittance of 0.03-0.04 at room temperature. The metal silicides and carbides are of interest for CSP applications, especially if an AR layer is added to increase the absorptance and the copper substrate is replaced with a stainless steel substrate to improve the thermal stability. Table 4 shows the absorptance, emittance and thermal stability of the sputter deposited mid-temperature solar selective coatings.

G.L. Harding also developed a new graded Cu-C cermet coating on copper substrates by sputtering a single Cu electrode in Ar+C_2H_2 and Ar plasmas. The coating exhibited absorptance of 0.94 and emittance of 0.04 at 120°C. This coating was thermally stable in vacuum at 500°C for 1 h [41]. Similarly, M. Sikkens developed a Ni-C cermet coating by sputtering a Ni target in Ar+CH_4 and Ar plasmas. Reactively sputtered Ni-C coatings deposited on Cu substrate exhibited solar absorptance of 0.78 and hemispherical emittance of 0.028 at 150°C. Solar absorptance of 0.90 and emittance of 0.045 have been obtained using sputtered Ni as a substrate. The thermal stability of the coatings was good up to 400°C in vacuum below 10^{-3} Pa [42].

Table 4. Absorptance, emittance and thermal stability of sputter deposited mid-temperature solar selective coatings.

Material	Substrate	α	$\varepsilon_{100°C}$	Stability		Refs.	Year
				Air (°C)	Vacuum (°C)		
Metal carbides	Bulk Cu	0.76-0.80	0.02-0.03	-	400 (120 h)	38	1976
Cr_2O_3/Cr with Cr_2O_3 ARC	Ni plated SS	0.92	0.08	300 (64 h)	-	48	1977
Au-MgO	Mo coated SS	0.90-0.93	0.10	400 (64 h)	-	49	1978
Metal silicides	Bulk Cu	0.75-0.81	0.02-0.03	-	400 (100-400 h)[a]	39	1978
Ge or Si-CaF_2	Quartz	0.70	0.07 at 500°C	-	<500	54	1979
Cu-Al_2O_3	Cu	0.86-0.90	0.03 at R.T.		<300	53	1979
Fe-SiO_2	Cu coated glass	0.91	0.03 at R.T	-	400 (100h)	53	1979
PbS with ZrO_2 ARC	Al coated glass	0.80	0.02	-	-	55	1982
Ni-C	Cu, Ni	0.80-0.90	0.02-0.04 at 150°C	-	400 (6h)	42	1982
Cu-C	Glass	0.94	0.04 at 120°C	-	500 (1h)	41	1982
Al/Al-C-F with Al-C-F ARC	Glass	0.93-0.97	0.07-0.08 at R.T.	- -	- -	45	1984
Al/Al-C-O with Al-C-F ARC	Glass	0.93	0.06 at R.T.		-		
Al/AlN	Glass	0.93	0.04 at R.T.	400		43	2006
Cu/SS-C-O/Al-C-F	Glass	0.93	0.03 at R.T.	-	-	45	1984
Cu/SS-C/a-C:H	Glass	0.94	0.03 at R.T.	-	-		

Continued……

Cu-SS-a-C	Glass	>0.90	<0.05 at 300°C	-	400 (4 h)	44	1985
TiNOx*	Cu	0.95	0.05	300	-	60	1993
Cr_2O_3/CrN**	Cu	0.93	0.07	250	-	58	1997
a-C:H/Cr***	Cu	0.92	0.08-0.09	220 (280 h)	-	34	1998
Ni-NiO****	Al	0.96	0.10	-	300	62	1998
$NiCrO_x$	SS	0.80	0.14	-	<200	56	2000
Cr-Cr_2O_3	Cu	0.90-0.94	0.04	-	-	50	2001
Cr_xO_y-Cr-Cr_2O_3	Cu	0.89-0.91	0.05-0.06	275 (50 h)	500 (2 h)	51	2008
Cr-Cr_2O_3	Cu	0.92-0.96	0.05-0.08	-	300-400 (1 h)	52	2009
Ti-TiN_xO_y	Cu	0.91	0.04	-	-	61	2003
SS/SS-N	Glass	0.91	0.06	-	-	46	2010

[a]Thermal stability depends on metal layer.

(Marketed by *Almeco-TiNOX; **Alanod® Solar; *** IKARUS Coatings; ****Sunstrip**).**

Wyon and Valignat have developed a spectrally selective coating by successively depositing an opaque Cu layer, a thin film of stainless steel and an amorphous carbon layer by non-reactive magnetron sputtering. This coating exhibited absorptance higher than 0.90 and emittance less than 0.05 at 300°C. The coatings were thermally stable in vacuum at 400°C for 4 h [44]. These coatings (i.e., Cu/C Ni-C and Cu/SS/a-C) were developed for evacuated tubular solar water collector applications. The interdiffusion between the layers and the outward diffusion of Cu and its subsequent oxidation resulted in degradation of the coatings (Cu/C and Cu/SS/a-C) at higher operating temperatures.

Harding et al. have developed a number of new sputtered selective coatings by computer simulation and by sputtering method [45]. These coatings have been produced using continuously graded or multilayer films of reactively sputtered aluminum-carbon-fluorine, aluminum-carbon-oxygen or aluminum-nitrogen composite materials as the absorbing layer and pure aluminum as the low emittance metal base layer. These coatings were deposited using a single aluminum cathode in the sputtering system. The selective surface which consists of SS-C absorbing layer with Al-C-F antireflection layer, deposited on top of Cu base layer exhibited an absorptance of 0.96 and emittance of 0.05 at 100°C. These coatings were developed for evacuated solar water collector applications. Recently, Juang et al. developed a SS-SSN coating by sputtering a single stainless steel target in Ar and Ar+N_2 plasmas. This coating exhibited an absorptance of 0.91 and emittance of 0.06 at 82°C. The thermal stability of the coating has not been reported [46].

Electrodeposited black chrome coatings have been widely studied and used for solar hot water applications [47]. Due to environmental concerns, an alternative method is required for preparing black chrome coatings. Sputter deposited chromium oxide cermet coating has been developed as an alternative for electrodeposited black chrome coating. Various concepts such as graded cermets, multilayer cermets and multilayer absorbers have been used to develop Cr-Cr_2O_3 coatings. In 1977-78, Fan and Spura developed and compared the sputter deposited Cr-Cr_2O_3 cermet with electrodeposited black chrome coating. They found that the electrodeposited coatings are actually Cr-Cr_2O_3 cermets comparable in composition and microstructure to the sputtered films. The sputter deposited Cr-Cr_2O_3 cermet with Cr_2O_3 antireflection coating deposited on nickel coated stainless substrates exhibited an α/ε(100°C) of 0.92/0.08 [48,49]. The Cr-Cr_2O_3 cermet was prepared by radiofrequency sputtering using a hot-pressed target containing 71 vol% Cr_2O_3 and 29 vol%

Cr. The coatings were thermally stable in air at 300°C for 64 h. Further increase in the temperature (i.e., 400°C for 60 h) resulted in delamination of the coating from the substrate due to the differences in thermal expansion coefficients. John .C. C. Fan also developed Au-MgO coatings by using a hot-pressed target with 75 vol% MgO and 25 vol% Au [49]. The coatings deposited on copper, aluminum, SS 304 and SS 304 coated with molybdenum exhibited absorptance in the range of 0.90-0.93. However, the emittance was 0.04 and 0.10 for coatings deposited on Cu and SS substrates, respectively. The coatings were thermally stable in air at 200°C for Cu substrate, 300°C for SS and Al substrates and 400°C for Mo coated SS. With stability between 200 and 400°C, Cr-Cr_2O_3 and Au-MgO coatings are potential candidates for solar hot water and industrial process heat applications.

Graded Cr-Cr_2O_3 cermets deposited on Cu and Al substrates exhibited high absorptance in the range of 0.90-0.94 and low thermal emittance of 0.04 [50]. Improvements in the coating performance are possible with the addition of an AR topcoat and if a metallic layer is used at the interface which acts as the IR reflector instead of the Cu or Al substrates. The sputter deposited Cr-Cr_2O_3 cermet is useful for low temperature applications, but is not useful for concentrating solar power applications.

Recently, our group has developed a Cr_xO_y/Cr/Cr_2O_3 multilayer absorber coating for mid-temperature solar thermal applications [51]. The Cr targets were sputtering using asymmetric bipolar pulsed dc generators in Ar+O_2 and Ar plasmas to deposit the multilayer absorber coating. The optimized multilayer absorber coating exhibited a high absorptance (0.899-0.912) and low thermal emittance (0.05-0.06). The coatings were thermally stable in air at 300°C. At higher temperatures, the absorptance decreased and the emittance increased drastically, which is due to the oxidation of Cr crystallites, increased surface roughness and the formation of CuO. There was no significant change in the absorptance and emittance values even after heating the coatings in vacuum at 600°C. Accelerated aging tests indicated that the coatings deposited on Cu substrates were stable in air up to 250 h at 250°C. The thermal stability of the coatings can be improved by depositing the coating on SS substrates.

Yin et al. have developed Cr-Cr_2O_3 multilayer cermets (with low-high-low metal volume fraction profile) by using the target current as a control parameter in optimization [52]. The solar absorptance of the sputtered black chrome selective surface was in the range of 0.92-0.96 and the thermal emittance was between 0.05 and 0.08. The coatings were

thermally stable at 300-400°C for 1 h. Long time aging at 170°C suggested that the coatings are suitable for solar hot water applications [52].

Similar to graded Cr-Cr_2O_3 cermets, graded Cu-Al_2O_3 cermets were also prepared on Cu substrates. The graded cermet coatings exhibited absorptance in the range of 0.86-0.90 and emittance of 0.031 at room temperature [53]. Annealing of the coatings in vacuum at 300°C resulted in a decrease in the solar absorptance from 0.86 to 0.83. This coating can be used for only low temperature solar applications due to its poor thermal stability.

Composite semiconductors such as Si-CaF_2 and Ge-CaF_2 were deposited on quartz substrates by co-sputtering method [54]. For solar thermal performance, quartz substrates were used with either evaporated gold-chrome or aluminum which was subsequently anodized providing the reflecting base for the composite layer. The coatings exhibited α = 0.70 and ε = 0.07 at 500°C.

Martin et al. has prepared PbS thin films by ion beam sputtering, electron beam evaporation and thermal evaporation methods and compared the optical properties of these coatings [55]. Thermally evaporated PbS coatings exhibited very high absorption when compared to the sputtered and electron beam evaporated coatings. This is due to the porous surface texture of thermally evaporated coatings. Addition of 60 nm evaporated ZrO_2 AR coating on 50 nm PbS film increased the absorptance from 0.66 to 0.80 and reduced the emittance from 0.08 to 0.024.

Reactively sputtered $NiCrO_x$ coating on SS substrate exhibits near zero reflectance at 0.8 μm and a high reflectance in the infrared region. The absorptance of the coating is 0.80 and the emittance is 0.14 at 60°C [56]. A sputtered Ni-Cr selective surface on polyamide substrate has $\alpha/\varepsilon_{60°C}$ = 0.92-0.93/0.06 and is stable for use under 200°C [57]. These coatings are useful for low temperature applications and are not suitable for concentrating applications.

3.1. Commercially available mid-temperature solar selective coatings

For solar hot water and industrial solar heat applications, various mid-temperature sputter deposited solar selective coatings have been developed and few of them have been successfully commercialized. SS-AlN, CrN-Cr_2O_3, eta plus, TiNOX, a-C:H/Cr, TiC/TiO_xN_y/AlN and Ni-NiO coatings are commercially marketed by TurboSun, Alanod Solar, BlueTec, Almeco-TiNOx, Ikarus Coatings, PLASMA and Sunstrip, respectively and

are discussed below. Table 5 gives a list of the commercially available sputter deposited coatings for mid temperature applications.

TurboSun, in conjunction with Peking University and the University of Sydney, has commercially developed evacuated solar collector tubes incorporating sputtered stainless steel–aluminum nitride cermet solar selective coatings. Currently, TurboSun manufactures three different series of solar collector tubes with superior solar performance in China. TurboSun also designs, manufactures and installs utility-scale solar hot water systems. TurboSun in China produced 3.5 million commercial U-shaped all-glass evacuated solar collector tubes for low temperature solar hot water collectors. These tubes are widely used for solar hot water and steam heater applications. According to the IEA report, the dominant collector type is the evacuated tube collector, which represents 54.2% of the global market followed by the flat-plate collector with a market share of 32.6% [5].

A spectrally selective coating with absorptance greater than 0.93 and emittance of 0.07 has been developed using experimental design methods by Graf et al. [58]. The graded cermet based on chromium oxynitride was deposited on Cu substrates by dc magnetron sputtering technique. The durability tests were carried out as an inter-laboratory comparison in the framework of the working group 'Materials in Solar Thermal Collectors' of the Solar Heating and Cooling Program of the IEA. The results showed that the graded CrN/Cr_2O_3 coating deposited on Cu sheets is durable enough for an application in ventilated flat plate collectors for domestic hot water system with a service life time of more than 25 years. These coatings were commercially produced by Alanod Solar and the product name is Sunselect®.

The three products, Sunselect®, Mirotherm and Mirosol are commercially marketed by Alanod Solar. Sunselect® (CrN/Cr_2O_3) is a cermet multilayer coating with a graded refractive index, where very small metallic particles are dispersed in an amorphous dielectric matrix. Chromium, which is one of the major metals used in this process is applied on top of the substrate as a barrier layer to prevent corrosion of the substrate and diffusion of the substrate material into the upper layers, which enhances the durability of the coating drastically. Sunselect® is durable and temperature resistant up to 300°C and it adheres firmly to the metallic substrate. The Mirotherm and Mirosol coatings are developed on aluminum substrates and the coatings exhibited thermal stability in air at 210-220°C.

Table 5: List of commercially available mid-temperature solar selective coatings.

Company	**Coating**	**Absorptance (α)**	**Emittance (ε)**	**Thermal Stability**
Alanod Solar (Germany)	Sunselect (Cu) (CrN-Cr_xO_y) Mirotherm® (Al) Mirosol® (Al)	0.95 0.95 0.90	0.05 0.05 0.15	-
TurboSun (China)	W-AlN SS-AlN	0.92-0.94 0.94-0.95	0.08-0.10 (350°C) 0.12-0.14 (350°C)	350-500°C in vacuum
BlueTec (Germany)	eta Plus (Cermet coating)	0.95	0.05	295°C
Almeco-TiNOX (Germany)	TiNOX Classic Vega AB127	0.95 0.95	0.04 0.05	- -
Sunstrip (Sweden)	Ni-NiO	0.96	0.10	300°C
PLASMA (Macedonia)	$TiC/TiO_xN_y/AlN$	0.95	<0.10	350°C
IKARUS coatings (Germany)	a-C:H/Cr	0.92	0.08-0.09	250°C
SCHOTT Spezialglas (Germany)	ALUXID®	0.95	0.05	280°C

BlueTec GmbH (Germany) has developed a new generation absorber (eta plus) for solar hot water applications. The eta plus coating has very high absorptance (0.95) and low thermal emittance (0.05). The coating performance was evaluated by ISE, Fraunhofer Institute for Solar Energy Systems in Freiburg, Germany. Based on their results, eta plus can be used at collector stagnation temperatures up to 295°C without reducing the collector life [59].

TiNOX Classic, a commercial TiN_xO_y cermet on copper substrate is produced by an Italian-German company called Almeco-TiNOX [60]. TiNOX Classic has an absorptance of 0.93-0.97 and emittance of 0.02-0.06. The coating has passed the IEA Task X Service Lifetime and Performance Criterion Tests. Ion assisted deposition (IAD) has also been used to form dense uniform TiN_xO_y selective surfaces [61]. The performance of TiN_xO_y cermets may be improved, with the addition of an AR topcoat and an IR metallic layer, instead of Cu or Al substrates. TiNOX GmbH is currently known as Almeco-TiNOX GmbH due to its merger with the Almeco group. Their products are TiNOX Classic, TiNOX Artline, Vega SP 195 and Vega SP 198.

The Center for Plasma Technologies - PLASMA developed and produced spectrally selective coatings based on Cu and Al absorbers for hot water collectors. The coatings are based on titanium composites (i.e., $TiC/TiO_xN_y/AlN$) with other metals and gas ions. The coatings exhibited high thermal stability (450°C), corrosion stability and good optical properties ($\alpha = 0.95$; $\varepsilon < 0.10$).

Nickel-nickel oxide graded index coatings on aluminum substrates are commercially produced by Sunstrip (Sweden) [62-64]. The commercial absorber coating has a solar absorptance in the range of 0.94-0.96 and thermal emittance of 0.13-0.15. The coating consists of three layers: a nickel barrier layer, a selectively absorbing Ni-NiO layer and an AR coating. The coating has passed stability tests according to the procedures recommended by International Energy Agency Task X working group on accelerated life testing of solar energy materials. Sunstrip – a Sweden based company is the complete supplier of strips and absorber plates for solar thermal collectors. The four main products of Sunstrip are: i) strips for solar thermal collectors, ii) absorbers for solar thermal collectors, iii) full-plate absorbers – Lazerplate and iv) strips for waterborne climate system. The Swedish Testing and Research Institute has carried out a number of tests on Sunstrip's sputtered absorbers. The tests were conducted in accordance with the requirements and methods stipulated by IEA

Task X. The tests included checking the surface's durability against condensation, sulphur oxide and high temperatures. Sunstrip's test results were approved and the values correspond to a product life span of over 25 years.

Transition metal containing amorphous hydrogenated carbon films (a-C:H/TM, TM = Ti, Cr) or transition metal containing silicon-carbon films (a-Si:C:H/TM) have been produced by a combined PVD and plasma enhanced chemical vapor deposition (PECVD) process [36,37,65]. A solar absorptance of 0.876 and emittance of 0.061 have been achieved for non-optimized a-C:H/Ti coatings whereas, a-C:H/Cr exhibited an absorptance of 0.918 and emittance of 0.08-0.09. These coatings were commercially produced by IKARUS coatings, Germany.

The vendors using the various commercially available coatings for solar hot water applications are listed in Tables 6-11. It is clearly evident from the tables that CrN-Cr_2O_3 (i.e., Sunselect) coating is being widely used in Germany, Belgium, China, Poland, etc. In India, Akson Solar uses the Sunselect coating for flat-plate collector applications. Similarly, TiNOX coating has a worldwide market and is being used by vendors in USA, China, UK, etc. The eta plus coating is being used by vendors mostly in Poland and China. SS-AlN coating has been widely marketed in China and this coating is mainly used in evacuated tube collectors for solar hot water applications. Al-AlN coating has few vendors and the coating is mainly used in ETC. In India, Jain Solar water heater uses Al-AlN coating for hot water applications. The Ni-NiO coating also has vendors in Ireland, Germany, etc. and this coating is used in FPC.

Table 6: List of vendors using the commercially available "Sunselect" coating for solar hot water applications.

Coating	Manufacturer	Model	Type
CrN-Cr_2O_3 (Sunselect)	Consolar, Germany	Plano 26	FPC
	European Solar Engineering, Belgium	ECOSOL	FPC
	Akson Solar, India	Sunselect	FPC
	Rotex, Australia	Rotex Solaris	FPC
	Strelbelwerk, Germany	Strebel	ETC
	Dietrisol, France	Dietrisol Pro	FPC
	Centrometal Heating Technique, Croatia	CPK 7210N	FPC
	Grant Solar, UK	Aurora and Sahara	FPC
	Ecopipe, Dublin	Sunstar 20 and Sunstar 30	ETC
	Ensol Komfort, Poland	ES1V2	FPC
	Careyglass Solar, Ireland	Careyglass	FPC
	Inno Water Heater Co. Ltd, China	Sunselect	FPC, ETC
	Ningbo Euro Solar Group Co. Ltd, China	EUSOLAR	ETC
	Energy and Environment Ltd., UK	Schuco Solar	FPC
	Regulus, Czech Republic	KPS10-ALP	FPC
	Boss Solar, Canada	Boss Solar	FPC

FPC – Flat Plate Collector; ETC – Evacuated tube collector

Table 7: List of vendors using the commercially available "TiNOX" coating for solar hot water applications.

Coating	Manufacturer	Model	Type
TiNOX	Consolar GmbH, Germany	Plano 26	FPC
	Regulus, Czech Republic	KPA1-ALP	FPC
	Haier, China	PGT2.0-2	FPC, ETC
	Powerlite Global, Malasiya	Solarpower™	ETC
	Kingspan Solar, UK	Marvel	FPC, ETC
	Solar Hot, USA	Solarhot Platinum Series	FPC
	Rinnai, Malaysia	Enduro Panel	FPC
	Aquaheat, Australia	Aquaheat	FPC
	Inno Water Heater Co. Ltd, China	TiNOX	FPC
	Erjin Solar, China	TiNOX	FPC, ETC
	Guangzhou Hopesun Solar Co. Ltd, China	Hopesun	FPC
	SOLEUAE, UAE	Climasol	FPC
	Techsun, USA	TiNOX Blue	FPC
	Sunsiaray, USA	Northern Comfort	FPC
	Sunflower Renewable Energy, China	Sunline	FPC
	Synergy Solar , USA	TiNOX Blue	FPC
	ONOSI, China	ONS-FBP01	FPC
	Tuttoclima, Italy	Suntherm	FPC

FPC – Flat Plate Collector; ETC – Evacuated tube collector

Table 8: List of vendors using the commercially available "BlueTec eta Plus" coating for solar hot water applications.

Coating	Manufacturer	Model	Type
BlueTec eta Plus	Kospel, Poland	BlueTec	FPC
	Euroterm, Macedonia	ESK2.5 SBT	FPC
	Regulus, Czech Republic	KPS11-ALP	FPC
	Haier, China	PGT2.0-2	FPC, ETC
	Inno Water Heater Co. Ltd, China	BlueTec	FPC
	SolarEko, Poland	WATT 3000 Su	FPC
	Ensol Komfort, Poland	Ensol ES1V/2	FPC
	RADSOL, Poland	WATT CPC Duo Medium	FPC
	PHNIX, China	PHNIX	FPC
	Zhejiang Gaodele Solar Energy Co., Ltd, China	GAODELE	FPC
	Gorenje, Hungary	BlueTec2	FPC
	Ateliving Trade and Industries Co. Ltd, China	BP2B-3	FPC
	Creative Solar Energy Co. Ltd, China	BlueTec	FPC
	WTO Solar, China	WTO-HFA	FPC

FPC – Flat Plate Collector; ETC – Evacuated tube collector

Table 9: List of vendors using the commercially available "SS-AlN" coating for solar hot water applications.

Coating	Manufacturer	Model	Type
SS-AlN	Jiangsu Sunpower Solar Technology Co. Ltd, China	Sunpower	ETC
	Interma, China	Interma-CPCO	ETC
	Jinyi Solar, China	JNA	ETC
	Shanghai Green Power Solar Technology, China	Evacuated Solar Collector Tube	ETC
	Runsun Energy, China	RUC	ETC
	Beijing Sunda Solar Energy Technology, China	SEIDO	ETC
	Future Sun Energy, China	WLYG-16	ETC
	Haining Jianeng Solar Energy Industry Co. Ltd, China	JNSC-12-58/1800	ETC
	Zhejiang Yudi New Energy Co. Ltd, China	Rise Top	ETC
	Inlight, China	VCSC	ETC
	Xianke Solar Energy Technology, China	XKHP 58	ETC
	Kelaibeier, China	Three Target Vacuum Tube	ETC
	Tianho Solar Technology, China	Integrated Pressurized Solar Water Heater	ETC
	Jiaxing Bojia Solar Energy Technology Co. Ltd, China	SDIJ-VC-1	ETC
	Haining Sunfull Solar Technology, China	Three Target Vacuum Tube	ETC
	Jishen, China	JSNP-019	ETC
	Haining Jixiang Solar Energy Co. Ltd, China	Evacuated Collector 12-58	ETC

Table 10: List of vendors using the commercially available "Al-AlN" coating for solar hot water applications.

Coating	Manufacturer	Model	Type
Al-AlN	Apricus, China	Apricus	ETC
	Jain Solar Water Heater, India	ETC	ETC
	Interma Solar Water Heater, China	Al-AlN	ETC
	Beijing Sunda Solar Energy Technology, China	SEIDO1	ETC
	Future Sun Energy, China	Single Target Vacuum Tube	ETC
	KEDCO Plc, Ireland	Evacuated Tube Solar Collector	ETC

Table 11: List of vendors using the commercially available "Sunstrip Absorber" for solar hot water applications.

Coating	Manufacturer	Model	Type
Ni-NiO	Weishaupt, Germany	Sunstrip	FPC
	LIR-Solar, Ireland	Sunstrip	FPC
	Arcon Solar, Denmark	Arcon Solar HT	FPC
	Solid Asia Pvt. Ltd, Singapore	Gluatmugl	FPC
	KEDCO Plc, Ireland	KEDCO	FPC

4. High temperature solar selective coatings

4.1. Metal-dielectric composite coatings

Thornton and Lamb investigated three coating configurations of Pt-Al_2O_3 cermets: (1) Pt-Al_2O_3 cermet with a linearly graded platinum content and an Al_2O_3 AR layer, deposited on platinum coated glass, (2) Pt-Al_2O_3 coating with a uniform platinum content and an Al_2O_3 AR layer, prepared on Pt, Cr and Mo coated glass and (3) Al_2O_3/M/Al_2O_3 (AMA) coating in which the M layer is made of a uniform Pt-Al_2O_3 cermet, deposited on Pt, Cr and Mo coated glass [66]. All the three configurations exhibited an absorptance greater than 0.90. For the graded and AMA configurations emittance less than 0.10 was obtained whereas, for the uniform cermet emittance was 0.13. Coatings deposited on platinum coated glass substrates were stable at 600°C in air for as long as 200 hrs. Whereas coatings deposited on Cr or Mo coated glass substrates were less stable, however, they showed promise for many applications in the temperature range of 300-500°C [66,67]. Tables 12-15 show the absorptance, emittance and thermal stability of the sputter deposited high temperature solar selective coatings.

Vien et al. have prepared Pt-Al_2O_3 cermet coatings on SS and superalloy substrates by rf co-sputtering [68]. The coatings exhibited an absorptance of 0.92 and an emittance of 0.14. The coatings deposited on SS and superalloy substrates were thermally stable at 400 and 600°C in hydrogen atmosphere, respectively. Pt-Al_2O_3 and Al_2O_3/$MoSi_2$ multilayer cermet coatings were prepared by rf-magnetron sputtering for high temperature solar applications. These coatings were optimized by computer simulation [69]. The tetragonal-$MoSi_2$/Al_2O_3 multilayers have solar absorptance up to 0.92 and emittance of 0.15 (1100 K). A high solar absorptance of 0.95 and emittance of 0.10 have been achieved for Pt-Al_2O_3 multilayers. These coatings were thermally stable in air at 600°C for 400 h. These coatings are promising candidates for high temperature solar applications. Even though Pt based solar selective coatings have been studied widely, the coatings were not commercialized due to the high cost of platinum.

A low cost selective coating (i.e., Mo/Fe-Al_2O_3/Al_2O_3) for the photo thermal conversion of solar energy at high temperatures was developed by Sella et al. High absorptance of 0.95 and low emittance of 0.05 (300 K) were achieved for this three layer stack. The coating deposited on stainless steel substrate was stable up to 400-500°C, while the coating deposited on superalloy substrates (Nicral, IN 100) was stable up to 600°C [70].

The cost of this coating is very low compared to Pt-Al_2O_3 coatings. Various other cermet coatings such as Cr-SiO, Ni-SiO_2, Mo-SiO_2, Fe-SiO_2, Ni-Al_2O_3, W-Al_2O_3, etc. have been developed for high temperature applications and are discussed below.

Cr-SiO cermets on Cu and Cr/Cu substrates were investigated for high-temperature solar applications [10]. The coatings exhibited absorptance in the range of 0.85-0.95 and emittance in the range of 0.027-0.085 (380 K). Aging studies in the temperature range from 400-800°C in an argon atmosphere for 1000 h (42 days) show that the structural changes within the first day of annealing and then remains constant [10]. Graded Fe-SiO_2 cermets were deposited on Cu coated glass substrates by dual cathode DC magnetron sputtering method. The coating exhibited absorptance in the range of 0.89-0.91 and emittance of 0.037-0.038 at room temperature, and is stable in vacuum up to 500°C. The stability of the Fe-SiO_2 cermet in vacuum suggests its use as a high temperature solar selective coating for evacuated collectors [53].

Farooq et al. developed a graded index Ni-SiO_2 cermet coating on Al and Cu substrates by co-sputtering method. Solar absorptance of 0.90-0.96 and emittance of 0.03-0.14 was achieved for Ni-SiO_2 coatings with SiO_2 AR coating [73]. The antireflection coating minimizes the optical interference effects within the film and increases the solar absorptance by 4% (from 0.92 to 0.96). They also developed various multilayer metal-dielectric graded index solar selective coatings in which the metal volume fraction increases with depth from top (AR coating) to bottom (film-substrate interface) [71-74]. The optimization studies were done on four layers V-Al_2O_3, W-Al_2O_3, Cr-Al_2O_3, Co-Al_2O_3, V-SiO_2, Ni-SiO_2, W-SiO_2 and Cr-SiO_2 cermets, where the metal volume fractions vary from 0.5 to 0.8.

Graded Ni-Al_2O_3 cermet coatings (650 Å thick) on molybdenum-coated nickel plated stainless steel with 780 Å thick SiO_2 AR coating was developed by T.S. Sathiaraj et al. These coatings exhibited an absorptance of 0.94 and an emittance of 0.07 [75]. Coatings without SiO_2 AR coating were thermally stable in air up to 400°C, whereas coatings with protective SiO_2 layer were stable up to 500°C in air for 1000 h.

Table 12: High-temperature solar selective coatings – Single layer cermets

Material	**Substrate**	**α**	**$\varepsilon_{(100°C)}$**	**Stability**		**Refs.**	**Year**
				Air (°C)	**Vacuum (°C)**		
Single Layer Cermets							
Pt-Al_2O_3 with Al_2O_3 ARC	Pt, Cr, Mo coated glass	0.89-0.91	0.13-0.14 at 20°C	400-600 (100h)	-	67	1981
Pt-Al_2O_3 with Al_2O_3 ARC	Mo or W coated SS	0.92	0.14 at 300°C	400 (H_2) (50-60h)	-	68	1985
	Mo or W coated superalloy	0.92	0.14 at 300°C	600 (H_2) (36-50h)	-	68	
Fe-Al_2O_3 with Al_2O_3 ARC	SS	0.95	0.14 at 427°C	400-500 (36 h) ($Ar+H_2$)	-	70	1987
	Superalloy			600 ($Ar+H_2$)			
Ni-Al_2O_3 with SiO_2 ARC	Mo-Ni-SS	0.94	0.07	500 (1000h)	-	75	1990
Cr-SiO	Cu, Cr/Cu	0.80-0.96	0.02-0.12	400-600 (Ar) 450 (28 days)	400-600 (28 days)	76	1987
ZrO_xN_y*	Ag coated glass and SS	0.88-0.93	0.08-0.30 at 327°C	-	600 (500 h)	77	1977

***single layer absorber (not a cermet)**

Table 13: High-temperature solar selective coatings – Double layer cermets

Material	Substrate	α	$\varepsilon_{(100°C)}$	Stability		Refs.	Year
				Air (°C)	Vacuum (°C)		
W-AlN with AlN ARC	Al coated Cu	0.92-0.94	0.08-0.10 at 350°C	-	500 (1 h)	85	1997
SS-AlN with AlN ARC	Al coated glass	0.94-0.95	0.12-0.14 at 350°C	-	330-400	84	1998
Mo-AlN with AlN ARC	Cu	0.92-0.94	0.08-0.10 at 350°C	-	350-500	86	2000
Ni-SiO_2	Al and Cu	0.90-0.96	0.03-0.14	-	-	73	1998
Mo-Al_2O_3	-	0.94	0.05	-	-	78	2002
Mo-SiO_2	SS	0.94	0.13 at 580°C	-	580 (6 h)	92	2009

Table 14: High-temperature solar selective coatings –Multilayers/Graded cermets

Material	**Substrate**	**α**	**$\varepsilon_{(100°C)}$**	**Stability**		**Refs.**	**Year**
				Air (°C)	**Vacuum (°C)**		
Al_2O_3-(Pt-Al_2O_3)-Al_2O_3	Pt, Cr, Mo coated glass	0.89-0.91	0.13 at 20°C	450-500 (100h)	-	67	1981
Al_2O_3/M/Al_2O_3 (M-Ni, Cr, Ta, Pt and Mo)	Glass	0.89-0.95	0.14-0.25 at 537°C	300-600* (100-150 h)	400-700*	79	1982
Pt-Al_2O_3 multilayers	Quartz,	0.95	0.08-0.20 at 827°C	700 (300 h)	-	69	1994
Al_2O_3/Cu/Al_2O_3/AlCuFe homogeneous/Al_2O_3	Cu coated Si wafer	0.890.90	0.04-0.06 at 400°C	400 (450 h)	-	89	1998
Al_xO_y-AlN_x-Al	Quartz glass	0.94-0.97	0.07	-	400-600 (30 min)	88	2003
Mo-Al_2O_3	SS	0.91-0.93	0.19-0.27	-	500 (2 h)	80	2008
Al_xO_y-Al-Al_xO_y	Cu Mo	0.95-0.97 0.93-0.95	0.05-0.08 0.05-0.09	400 (2 h) 400 (2 h)	- 800 (2 h)	90	2009
Mo/HfO_x/Mo/HfO_2	Cu	0.90-0.92	0.07-0.09	400 (2 h)	600 (2 h)	91	2010
W/W-Al_2O_3/Al_2O_3	SS	0.93	0.10 at 400°C 0.14 at 550°C	-	580 (30 days)	93	2010
NREL #6A	SS	0.95	0.08 at 500°C	500	-	96,97	2005
NREL #6B	SS	0.95	0.10 at 500°C	500	-	96,97	2005

*Thermal stability depends on metal (M) layer and Al_2O_3 deposition conditions

Table 15: High-temperature solar selective coatings – Tandem absorbers

Material	**Substrate**	**α**	**$\varepsilon_{(100°C)}$**	**Stability**		**Refs.**	**Year**
				Air (°C)	**Vacuum (°C)**		
TiAlN/TiAlON/Si_3N_4	Cu SS	0.93-0.94 0.93-0.95	0.05-0.08 0.15-0.17	550 550	600 -	101-105	2006
TiAlN/AlON	Cu	0.93-0.94	0.05-0.06	550 (2 h)	800 (2 h)	106	2008
NbAlN/NbAlON/Si_3N_4	Cu	0.93-0.95	0.07	500 (2 h)	600 (2 h)	107	2008
TiAlN/CrAlON/Si_3N_4	Cu	0.94-0.95	0.05-0.07	500 (2 h)	800 (2 h)	108	2008
TiAl/TiAlN/TiAlON/ TiAlO	SS, Cu	0.90	0.09-0.19	650 (1 h)	-	109	2009
Ti_xAl_{1-x}/TiN/$(TiN\text{-}AlN)_H$/ $(TiN\text{-}AlN)_L$/AlN	Polished SS	0.943	0.08	400 (2 h)	-	111	2010

Zhang et al. developed a double layer Mo-Al_2O_3 cermet coating on molybdenum or Cu substrates by rf sputtering method. The coating exhibited good optical properties $\alpha/\varepsilon_{350°C}$ = 0.96/0.16 for 350°C < T < 500°C in vacuum [81]. Whereas, vacuum evaporated Al_2O_3/Mo/ Al_2O_3 (AMA) coating on Mo substrate with $\alpha/\varepsilon_{500°C}$ = 0.85/0.11 was stable for 500 h at 920°C in vacuum [82]. At temperatures of ~900°C, the AMA coating on a Mo-coated SS substrate breaks down because of the diffusion of Fe and Cr from steel. The AMA coating has good thermal stability in vacuum, but the coating exhibited limited durability when exposed to air (i.e., thermally stable in air at 400°C for 24 h). Double layer cermet coatings of W-AlN, SS-AlN and Mo-AlN were also developed by the same group by reactive DC magnetron sputtering [83-87]. A solar absorptance of 0.92-0.94 and emittance of 0.08-0.10 at 350°C were achieved for the W-AlN and Mo-AlN cermet coatings. SS-AlN double-cermet layer coatings have $\alpha/\varepsilon_{100°C}$ = 0.95/0.05 and $\alpha/\varepsilon_{350°C}$ = 0.96/0.10 [84]. These coatings are thermally stable at 350-500°C in vacuum and are lower in cost than the Siemens concentrated solar power (CSP) tubes (formerly Solel tubes).

It is evident from Tables 12-14 that Al_2O_3 and AlN are the most widely used dielectric materials in cermet coatings. Yue et al. developed an Al_xO_y-AlN_x-Al tandem absorber for high temperature applications. The coating deposited on quartz substrates exhibited absorptance of 0.82-0.97 and emittance of 0.07-0.10. The coatings were thermally stable at 400-600°C in vacuum. Even after heating the coating at 550°C for 40 h, the absorptance was 0.98 and the emittance was 0.12 [88].

Solar selective absorbers based on AlCuFe thin films (i.e., Al_2O_3/Cu/Al_2O_3/AlCuFe homogeneous/Al_2O_3) and a cermet of AlCuFe particles embedded in an Al_2O_3 matrix (Al_2O_3/Cu/Al_2O_3/AlCuFe cermet/Al_2O_3) were deposited on Cu coated Si wafers by sputtering method [89]. The absorptance of the homogeneous films was found to be 0.89-0.90 and the emittance was 0.04-0.06 at 400°C. Whereas, for the cermet layer, the absorptance and emittance were 0.79 and 0.033, respectively at 400°C. The coatings were thermally stable in air at 400°C for 100 hrs.

Our group developed a spectrally selective Al_xO_y/Al/Al_xO_y multilayer absorber coating on copper (Cu) and molybdenum (Mo) substrates using a pulsed sputtering system [90]. The compositions and thicknesses of the individual component layers were optimized to achieve high solar absorptance (α = 0.950–0.970) and low thermal emittance ($\varepsilon_{82°C}$ = 0.05–0.08). The multilayer absorber deposited on Cu substrates exhibited high solar selectivity

(α/ε) of 0.901/0.06 even after heat-treatment in air up to 400°C for 2 h. At 450°C, the solar selectivity decreased significantly on Cu substrates (e.g., α/ε = 0.790/0.07). Studies on accelerated aging tests suggested that the absorber coatings on Cu were stable in air up to 75 h at 300°C and the service lifetime of the multilayer absorber was predicted to be more than 25 years.

Table 16. Commercially available high temperature solar selective coatings

Company	**Coating**	**Absorptance (α)**	**Emittance (ε)**	**Thermal Stability**
Angelantoni-ENEA (Italy)	Mo-SiO_2 W/W-Al_2O_3/Al_2O_3	0.94 0.93	0.13 (580°C) 0.10 (400°C) 0.14 (550°C)	580°C in vacuum
Solel (Israel)	UVAC 2008 (Al_2O_3 based cermet)	0.96	0.10 (400°C)	400°C
	Mo-Al_2O_3	0.96	0.16 (350°C)	350-500°C in vacuum
	W-Al_2O_3	0.96	0.16 (350°C)	350-500°C in vacuum
SCHOTT	HTC	0.95	0.10 (400°C)	500°C in vacuum

Solar selective coatings of HfO_x/Mo/HfO_2 were deposited on Cu and SS substrates using a magnetron sputtering system [91]. The optimized HfO_x/Mo/HfO_2 multilayer absorber on Cu substrate exhibited high solar absorptance (α = 0.905–0.923) and low thermal emittance ($\varepsilon_{82°C}$ = 0.07–0.09). Similarly, on SS substrates the optimized coatings exhibited α and $\varepsilon_{82°C}$ in the range of 0.902–0.917 and 0.15–0.17, respectively. The HfO_x/Mo/HfO_2 coatings deposited on Cu substrates were thermally stable up to 400°C for 2 h in air. Addition of a thin Mo interlayer (40 nm) in the HfO_x/Mo/HfO_2 coating (i.e., Mo/HfO_x/Mo/HfO_2) deposited on Cu substrates exhibited high solar selectivity (α/ε) of 0.872/0.09 even after heat-treatment in air up to 500°C for 2 h. The Mo/HfO_x/Mo/HfO_2 coatings deposited on SS substrates showed no significant changes in α and ε values after annealing at 500°C in air and at 800°C in vacuum.

Recently, Mo-SiO_2 and W-Al_2O_3 graded cermet coatings have been fabricated for the receiver tube of solar parabolic trough plants [92-95]. This work is related to ENEA Solar

Thermodynamic Project, where the thermal exchange fluid is a molten salt entering at 290°C in the solar field and coming out at 550°C. Therefore, the receiver tube and the solar coating have to be very stable up to 580°C. Solar absorptance greater than 0.94 and emittance lower than 0.13, at 580°C have been obtained for graded Mo-SiO_2 coatings. Whereas, graded W-Al_2O_3 coatings have $\alpha/\varepsilon_{550°C}$ = 0.93/0.14 and both the coatings were thermally stable at 580°C in vacuum. Table 16 shows the list of commercially available high temperature solar selective coatings.

C.E. Kennedy, National Renewable Energy Laboratory (NREL), USA modeled a solar selective coating (NREL #6A) with absorptance of 0.959 and emittance of 0.06 at 400°C using a computer aided design software. NREL #6A coating is composed of multiple cermet layers (i.e., TiSi-a and TiO_2) and multiple AR layers (i.e., SiO_2) [96,97]. NREL also developed another high temperature solar selective coating (NREL #6B) with absorptance of 0.957 and emittance of 0.07 at 400°C. The difference between the models A and B is the substitution of TiSi-a by Pt. [96].

4.2. Tandem absorbers

In recent years, transition metal nitride and oxynitride coatings have attracted considerable research interest due to their exotic mechanical, chemical, electrical and optical properties. The optical properties of transition metal based nitride coatings can be tailored by controlling the stoichiometry, which affects the density of free electrons in the transition metal 'd' band [98,99]. Incorporation of an additional element (such as Al) in the transition metal nitride matrix changes the bonding structure (e.g., metallic to covalent). It is known that transition metal nitride (such as TiN, NbN, CrN, etc.) exhibits metallic character and AlN exhibits covalent character. The change in the bonding structure results in variations in the electrical resistivity and the optical properties of transition metal nitride based coatings. Transition metal-based nitride and oxynitride coatings such as TiAlN, TiAlON and TiNOX exhibit good optical properties. Schuler et al. reported that single layer TiAlN coating shows an absorptance of 0.8 and it can be used as a solar control window coating [98]. According to Luthier and Levy, TiAlON films displayed a low reflectance (below 16%) and high absorption coefficient ($1\text{-}4 \times 10^5$ cm^{-1}) in the visible-near ultraviolet spectral range [100].o

Recently, our group has developed a new generation high temperature tandem absorber of TiAlN/TiAlON/Si_3N_4 using a reactive DC magnetron sputtering process [101-103]. The optimized tandem absorber deposited on Cu substrates exhibited high absorptance

of 0.939-0.958 and low emittance of 0.05-0.07 at 82°C. The high solar absorptance is achieved by gradually decreasing the refractive index of the tandem absorber from the substrate to the surface [104]. This coating concept has been granted a US patent in 2009 (Patent No: 07585568) [105]. Heat treatment of the tandem absorber in air for 2 h at 625 °C did not significantly affect the absorptance (0.906) and the emittance (0.08). The high thermal stability of the tandem absorber is attributed to various factors. Firstly, TiAlN acts as a diffusion barrier for copper. It has been reported that the formation of TiO, AlN, and Al_5Ti_2 compounds during annealing of TiAlN/Cu at higher temperatures (800–1000 °C) effectively blocks the diffusion paths for Cu, thus making it an ideal diffusion barrier layer. Secondly, the interdiffusion between TiAlN/TiAlON and TiAlON/Si_3N_4 is expected to be very low up to 600 °C as TiAlN, TiAlON and Si_3N_4 are reported to have stable microstructures, high activation energies, and very high melting points. Finally, TiAlN, TiAlON and Si_3N_4 exhibit very high oxidation resistance: 750, 900 and 1400 °C, respectively [102]. The tandem absorber of TiAlN/TiAlON/Si_3N_4 therefore exhibits high thermal stability and oxidation resistance and retains its optical properties even at higher operating temperatures. At present, our group is working on scaling up the coating process and depositing coatings on 6" inch long SS tubes by a semi-industrial DC magnetron sputtering system, the photograph of which is shown in Figure 12(a). The photograph of the 6" long tube coated with TiAlN/TiAlON/Si_3N_4 coating is shown in Fig. 12(b). The study of long term stability of the coating and optimization of the process parameters to make the process economically viable is currently underway.

Our group has also developed various transition metal nitride based tandem absorbers such as TiAlN/AlON, NbAlN/NbAlON/Si_3N_4 and TiAlN/CrAlON/Si_3N_4 for high temperature solar selective applications [106-108]. High solar absorptance of 0.931-0.942 and low thermal emittance of 0.05-0.06 was achieved for optimized TiAlN/AlON tandem absorber deposited on copper substrate. The TiAlN/AlON tandem absorber deposited on Cu substrates exhibited high solar selectivity (α/ε) of 0.946/0.07 even after heat treatment in air up to 600 °C for 2 h. At 625 °C, the solar selectivity decreased significantly on Cu substrates (e.g., α/ε = 0.924/0.30). The tandem absorber on Cu substrates was also stable in air up to 100 h at 400 °C with a solar selectivity of 0.919/0.06 [106]. Similarly, the optimized NbAlN/NbAlON/Si_3N_4 tandem absorber deposited on Cu substrates exhibited absorptance in the range of 0.938-0.956 and emittance of 0.07 at 82°C. The coatings were thermally stable

in air at 500°C for 2 h and also found to be stable in air for longer durations (250°C for 350 h) [107]. The TiAlN/CrAlON/Si_3N_4 tandem absorber deposited on Cu substrates exhibited high solar absorptance in the range of 0.941-0.958 and low emittance of 0.05-0.07 at 82°C. Heat treatment of the tandem absorber in air for 2 h at 550°C did not affect the absorptance (0.927) and emittance (0.10) significantly. These tandem absorbers were also found to be stable in air for longer durations (300°C for 150 h) [108]. Due to their high thermal stability and good optical properties, all these tandem absorbers (i.e., TiAlN/TiAlON/Si_3N_4, TiAlN/AlON, NbAlN/NbAlON/Si_3N_4 and TiAlN/CrAlON/Si_3N_4) are potential candidates for CSP applications.

Spectrally selective TiAl/TiAlN/TiAlON/TiAlO coating was deposited on SS and Cu substrates by multi-arc ion plating system [109,110]. The coatings exhibited high absorptance of 0.90 and emittance of 0.08-0.19 and the coatings were thermally stable in air up to 650°C for 1 h. Hao Lei et al. also developed a TiAl/TiN/$(TiN\text{-}AlN)_H$/$(TiN\text{-}AlN)_L$/AlN on polished SS substrates by magnetron sputtering technique. The coatings were thermally stable in air at 500°C for 2 h with a solar selectivity of 0.948/0.08 [111].

(a)

(b)

Figure 12. Photograph of (a) semi-industrial magnetron sputtering system and (b) 6" long SS tube coated with TiAlN/TiAlON/Si_3N_4.

5. Commercially available solar receiver tubes used in parabolic trough collectors for solar thermal power generation applications

For solar thermal power generation, at present, parabolic trough technology is the most proven and low cost, large-scale solar power technology. Compared to other solar technologies, parabolic trough systems have the advantage of being established as a technology for installation at a commercial level. The first trough plant was installed in USA in the 1980's. Since then, they have undergone vast improvements both in terms of cost and efficiency. Parabolic trough systems currently have an installed capacity of 870 MW, with 2152 MW under construction and 10 GW in development. The worldwide status of parabolic trough power plants are described in Tables 17-22 [112,113].

Luz International Ltd., designed three generations of PTCs called LS-1, LS-2 and LS-3 which have been installed in Solar Electric Generating System (SEGS) plants. The heat collector element (i.e., absorber tubes) used in Luz collectors is a stainless steel tube with a special selective coating, enclosed under vacuum by a glass tube or envelope. Luz collectors used conventional glass-to-metal seals and metal bellows to achieve the vacuum-tight enclosure. The vacuum between the tubes is necessary to protect the selective coating against oxidation, reduce thermal losses, and to offset the differences in thermal expansion between the steel tubing and the glass envelope. The selective coating used in the LS-1and LS-2 collectors was black chrome, whereas, a new ceramic-metal layer (cermet; 0.3 μm thick) was applied by ionic bombardment under vacuum in the LS-3 collector.

The Solel Universal Vacuum Collector, which improved the original Luz absorber tube, but did not change the size, was successfully tested in the EuroTrough collector. Solel's UVAC 2008 (Figure 13) solar receiver is the world's most technologically advanced heat-collecting element for parabolic trough collectors. With its unique selective and antireflective coatings, the UVAC 2008 maximizes the heat absorption and keeps heat loss to an absolute minimum. In addition to this, Solel's patented getter system prevents the "hot tube" phenomenon which is due to hydrogen permeation, ensuring that the performance of the UVAC 2008 remains undiminished by high temperatures for 20 years [114]. UVAC is the world's best-selling solar receiver, with over 100,000 units successfully installed in the United States, Spain and Israel. UVAC uses a new Al_2O_3 based multilayer cermet, which has an absorptance of 0.97-0.98 and emittance of 0.07-0.10 at 400°C.

Table 17: Parabolic trough solar thermal power plants – USA (in operation).

Power Plant Manufacturer	CSP Plant Name	Collector/ Receiver tube Used	Capacity (MW)	Country/ Location	Year of Operation
Luz International Ltd.	SEGS I and II	LS1/LS2 collectors	43.8	USA/Mojave Desert, California	1984-1985
Luz International Ltd.	SEGS III -VI	LS2 collectors	120	USA/Mojave Desert, California	1986-1988
Luz International Ltd.	SEGS VII	LS2/LS3 collectors	30	USA/ Mojave Desert, California	1988
Luz International Ltd.	SEGS VIII and IX	LS3 collectors	160	USA/Mojave Desert, California	1989-1990
Acciona Solar Power and Siemens	Nevada Solar One	Solargenix SGX-1 parabolic trough collector; 62% Schott PTR70 & 38% Solel UVAC receivers	64	USA/Boulder City, Nevada	2007
Acciona Solar Power and ORMAT	Saguaro Solar Generating Station	SGX1 collectors; SCHOTT PTR 70 receiver tubes	1	USA/Arizona/Red Rock, near Tucson	2006
Sopogy	Holaniku, Keyhole Point	-	2	Kona, Hawai	2009

Table 18: Parabolic trough solar thermal power plants – Spain (in operation).

Power Plant Manufacturer	CSP Plant Name	Collector/ Receiver Tube Used	Capacity (MW)	Country/ Location	Year of Operation
ACS Cobra and Solar Millenium	Andasol I	SKAL-ET collectors; Schott receiver tubes	50	Spain/Guadix Plateau, Granada	2008
Iberdrola Energía Solar	Ibersol Puertollano	352 ET150 collectors; Solel UVAC receivers	50	Spain/Puertollano	2009
Acciona Solar Power	Alvarado I	SGX1 collectors	50	Spain/Badajoz	2009
Renovables SAMCA	La Dehesa	Ingemetal (SAMCA-Trough) collectors; Schott receivers	50	Spain/Badajoz	2010
Renovables SAMCA	La Florida	Ingemetal (SAMCA-Trough) collectors; Schott receivers	50	Spain/Badajoz	2010
ACS Cobra and Solar Millenium	Andasol II	SKAL-ET collectors; Schott receiver tubes	50	Spain/Guadix Plateau, Granada	2009
ACS/Cobra Group	Extresol I	UTE CT Extresol-1 (SENERTROUGH) collectors; Schott PTR 70 receivers	50	Spain/Badajoz	2009
Abengoa Solar	Solnova-I and Solnova III	360 ET150 collectors; Schott receiver tubes	100	Spain/Seville	2009

Table 19: Parabolic Trough Solar Thermal Power Plants – USA (under development).

Power Plant Manufacturer	CSP Plant Name	Collector/ Receiver tube Used	Capacity (MW)	Country/ Location
Florida Power and Light Company	Martin Next Generation Solar Energy Center	-	75	USA/Indiantown, Florida
Abengoa Solar	Solana	-	280	USA/Phoneix, Arizona
Mojave Solar, LLC; Abengoa Solar, Inc.	Abengoa Mojave Solar Project	-	250	USA/Harper Dry Lake, California
Solar Millenium, LLC; Chevron Energy solutions	Blythe Solar Power Project	-	250	USA/California
Genesis Solar	Genesis Solar Energy Project	-	250	USA/California

Table 20: Parabolic trough solar thermal power plants – Spain (under development).

Power Plant Manufacturer	CSP Plant Name	Collector/ Receiver Tube Used	Capacity (MW)	Country/ Location
ACS Cobra and Solar Millenium	Andasol III	Cobra Instalaciones y servicios (SENERTROUGH) collectors; Solel UVAC 2008 receivers	50	Spain/Aldeire/ Granada
ACS Cobra and Solar Millenium	Andasol IV	Cobra Instalaciones y servicios (SENERTROUGH) collectors; Solel UVAC 2008 receivers	50	Spain/Guadix Plateau, Granada
ACS/Cobra Group	Extresol II	Cobra Instalaciones y servicios (SENERTROUGH) collectors; Solel UVAC 2008 receivers	50	Spain/Badajoz
Abengoa Solar	Solnova-IV	360 ET150 collectors; Schott receiver tubes	50	Spain/Seville
Torresol	Arcosol 50	-	50	Spain/San José del Valle
Torresol	Vallesol 50	-	50	Spain/ San José del Valle
Bogaris	EL REBOSO II	SKALET 150 collectors	50	Spain/Sevilla
Bogaris	EL REBOSO III	SKALET 150 collectors	50	Spain/Sevilla

Contd..

Power Plant Manufacturer	CSP Plant Name	Collector/ Receiver Tube Used	Capacity (MW)	Country/ Location
ACS/Cobra Group	Extresol III	Cobra Instalaciones y servicios (SENERTROUGH) collectors; Solel UVAC 2008 receivers	50	Spain/Badajoz
Helios I HYPERION Energy Investments, S.L	Helios I	SCHOTT collectors	50	Spain/Arenas de San Juan, Villarta de San Juan, Puerto Lapice
Helios I HYPERION Energy Investments, S.L	Helios II	SCHOTT collectors	50	Spain/Arenas de San Juan, Villarta de San Juan, Puerto Lapice
Solucia Renovables	Lebrija (LE-1)	Solel receivers	50	Spain/Sevilla
Acciona Energía	Majadas I	Acciona Solar Power collectors	50	Spain/Majadas de Tietar
ACS/Cobra Group	Manchasol-1	Cobra Instalaciones y servicios (SENERTROUGH) collectors; Schott receivers	50	Spain/Alcazar de San Juan
ACS/Cobra Group	Manchasol-2	Cobra Instalaciones y servicios (SENERTROUGH) collectors; Schott receivers	50	Spain/Alcazar de San Juan
Acciona Energía	Palma del Rio I	Acciona Solar Power collectors	50	Spain/Palma Del Rio
Acciona Energía	Palma del Rio II	Acciona Solar Power collectors	50	Spain/Palma Del Rio

Table 21: Parabolic trough solar thermal power plants – India (planning).

Power Plant Manufacturer	CSP Plant Name	Collector/ Receiver Tube Used	Capacity (MW)	Country/ Location
Sunbourne Energy Ltd.	-	-	50	India/Gujarat
Entegra	-	-	30	India/Rajasthan
NTPC	-	-	25	India/Rajasthan
NTPC	-	-	15	India/Uttar Pradesh
Entegra*	Rajasthan Solar One	-	10	India/Rajasthan

*Under construction

Table 22: Parabolic trough solar thermal power plants – Other Countries (under development).

Power Plant Manufacturer	**CSP Plant Name**	**Collector/ Receiver Tube Used**	**Capacity (MW)**	**Country/ Location**
Abener	ISCC Argelia	Schott collectors	150 MW	Algeria/Hassi R'mel
NREA	ISCCS Al Kuraymat	-	140	Egypt/Al Kuraymat
Abener	ISCC Morroco	Schott collectors	470	Morocco/At Ain Beni
ENEL	Archimede Solar Power Plant	HEMS08 receiver tubes	5	Italy Near Siracusa, Sicily
Masdar/Total/ Abengoa Solar	Shams 1	-	100	United Arab Emirates
Under Planning				
Parsons Brinckerhoff	Kogan Creek	-	150	Australia-Kogan Creek, Queensland
CSIRO	-	-	200	Australia
CAMDA New Energy	-	-	1	China/Guangdong
Inner Mongolia Ruyi Industry Co.Ltd + Solar Millenium	-	-	1000 (50)	China/Ordos, Innner Mongolia

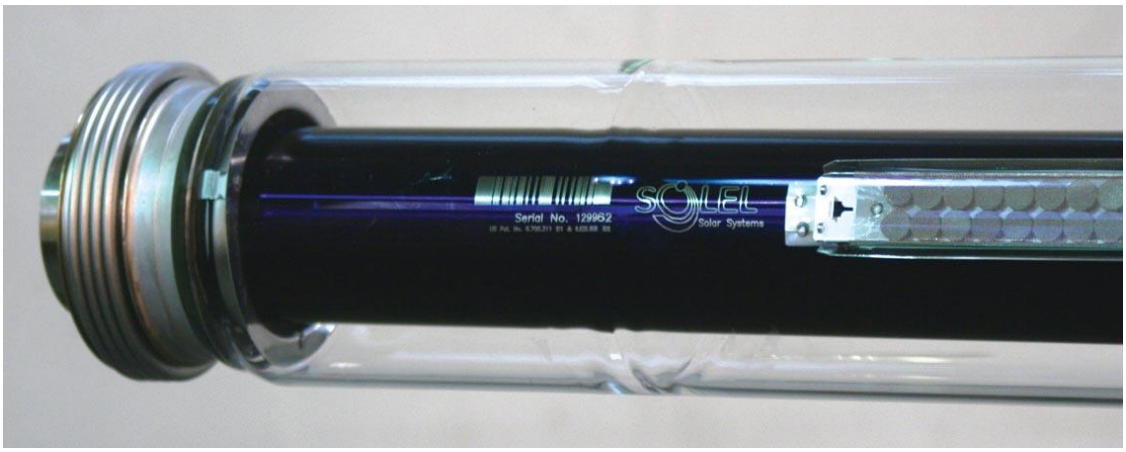

Figure 13. Photograph of UVAC 2008 receiver tube used in the parabolic trough power plants for solar thermal power generation.

Solel Solar Systems Ltd. which is currently known as Siemens Energy released a new solar receiver, the UVAC 2010, which further increases thermal heat production. The salient features of UVAC 2010 are extremely high solar absorption, reduced heat loss and an enlarged active area, offering solar field developers significantly increased revenues and reduced operating costs. UVAC 2010 features low emissivity as a result of technological advances in the sputtered selective coatings, as well as an improved active area to length ratio, which enables greater solar exposure of the receiver and a proportionate increase in absorbed energy [114]. The commercially available receiver tubes used in parabolic trough power plants for solar thermal power generation are given in Table 23.

In the past, Solel Solar Systems Ltd. was the only manufacturer of commercially available replacement heat collection element. Recently, Archimede solar energy (ASE) and Schott began producing collector tubes. Archimede Solar Energy (ASE) produces receiver tubes for thermodynamic solar power plants licensed by ENEA. ASE's HEMS08 (Figure 14) is the world's most advanced solar receiver tube, designed for thermodynamic solar power plants, operating at high temperatures (up to 550°C) with molten salt as heat transfer fluid. Archimede Solar Energy is the world's only company that uses molten salt as heat transfer fluid in its solar receivers for parabolic-trough power plants [115]. The efficiency of power plants using molten salt as HTF is higher than those using the synthetic aromatic fluid. Molten salt can also be used as a heat store, with the stored energy being used in solar thermal power plants to produce electricity at night. Solar receiver tubes coated with

selective coatings (i.e., Mo-SiO_2 and W-Al_2O_3) have an absorptance greater than 0.95 and emittance of 0.10 at 400°C and 0.14 at 580°C.

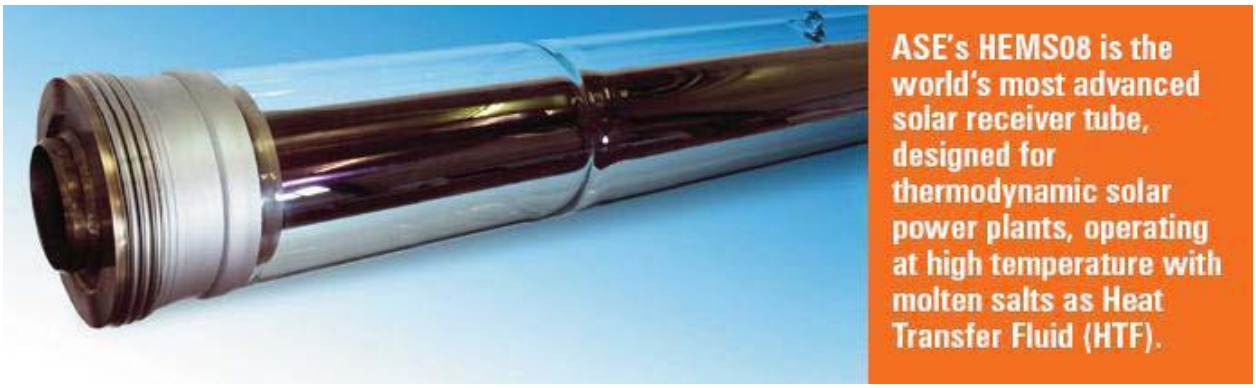

Figure 14. Photograph of HEMS08 receiver tube used in the parabolic trough power plants for solar thermal power generation.

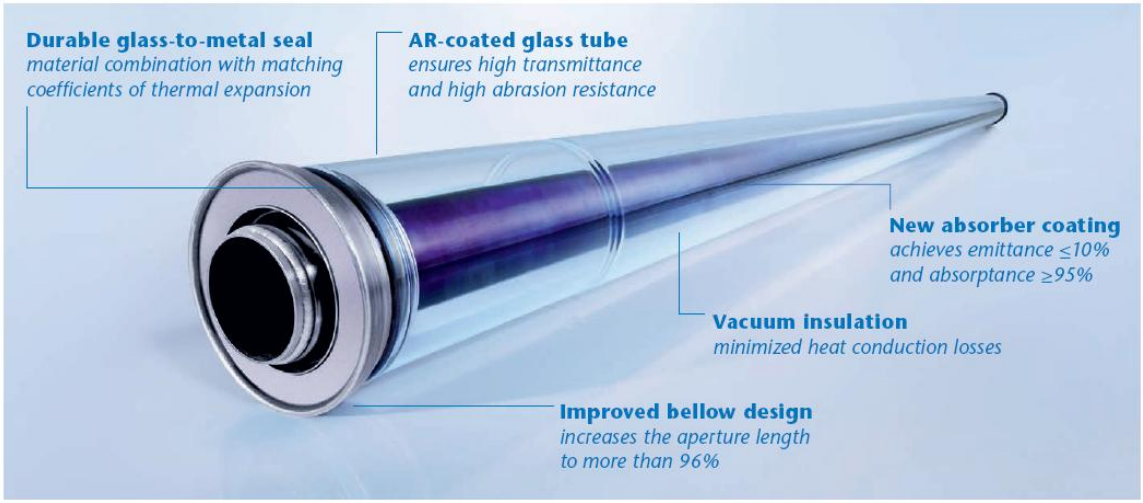

Figure 15. Photograph of SCHOTT PTR 70 receiver tube used in the parabolic trough power plants for solar thermal power generation.

The Schott receiver uses a selective coating similar to the original Luz Mo-Al_2O_3 cermet. The SCHOTT ICR® collector tube with ALUXID® absorber is made almost entirely of glass, a corrosion proof and easily recyclable raw material. The circular silver mirror on the inner surface of the envelope tube (i.e. ICR – Internal Circular Reflector) reflects all the incident radiation on the aperture of the envelope tube to the absorber tube. The selective absorber coating ALUXID® is applied to the inner glass tube by means of a magnetron sputtering process. This multilayer coating efficiently converts solar radiation into heat and

at the same time ensures reduced thermal radiation losses. The coating has absorptance of 0.94-0.96 and emittance of 0.03-0.07. These tubes are designed to withstand a stagnation temperature of 280°C [116].

The SCHOTT PTR® 70 (Figure 15) receiver tube has a new type of anti-reflection coating which has a high abrasion resistance and at the same time allows the transmission of more than 96 percent of the sun's radiation [116]. The absorber coating has an absorptance of 0.95 and very low emittance of below 0.10 at a temperature of about 350-400°C [116]. The glass-to-metal sealing and the bellow, that is necessary to compensate the different expansion of glass and metal, are not arranged in succession (as it is common in other collector tubes) but on top of each other. This means that about 96 percent of the receiver's length is actually used for conversion process. Comparison measurements by "Deutsches Zentrum für Luft- und Raumfahrt" (DLR) on the "Plataforma Solar de Almería" testing grounds in southern Spain have confirmed that the SCHOTT PTR® 70 receiver is 2% more efficient than other commercial tubes.

Table 23: Commercially available receiver tubes for parabolic trough power plants.

Manufacturer	**Receiver Name**	**Receiver Tube dimensions (mm)**	**Operating pressure (bar)**	**Operating temperature (°C)**	**Heat transfer fluid**
Solel Solar System	UVAC 2008	Length: 4060 mm; OD: 70 mm and thickness: 3 mm	-	400	Synthetic aromatic fluid
Schott	PTR 70	Length: 4060 mm; OD: 70 mm and thickness: 3 mm	≤ 40	400	Synthetic aromatic fluid
HEMS08	Archimede Solar Energy	Length: 4060 mm; OD: 70 mm and thickness: 3 mm	20	580	Molten salt (60% KNO_3+40%$NaNO_3$)

6. Future scope and summary

Solar thermal energy is expected to emerge as an important source of renewable energy for meeting the ever-increasing energy requirements of the world. In this regard, there is an increasing demand for solar selective coatings (or) spectrally selective coatings for mid-temperature and high-temperature solar thermal applications. Deposition of solar selective coatings by the sputtering technique is gaining momentum particularly due to the rising environmental concerns. A large variety of solar selective coatings have been explored over the past years and many novel coatings have been prepared in recent years to meet the requirements of mid-temperature and high-temperature applications.

Various mid temperature solar selective coatings such as SS-AlN, CrN-Cr_2O_3, eta Plus, TiNOX, Al-AlN, Ni-NiO, a-C:H/Cr, etc. have been developed and are being commercially used for solar hot water applications. Among these, TiNOX coatings have a worldwide market and SS-AlN coatings have a huge market in China. SS-AlN coatings have high thermal stability in vacuum (i.e., 300-500°C) but these coatings are mainly used in evacuated tube collectors for solar hot water applications. Sputter deposited chromium-chromium oxide coatings are one of the potential candidates for solar hot water applications but the coating has not been commercialized like electrodeposited black chrome coatings.

At present, development of sputter deposited solar selective coatings for high-temperature applications need considerable attention. Furthermore, efforts should also be aimed at preparation of solar selective coatings by sputtering on large areas at affordable costs. The present survey clearly shows that the Pt-Al_2O_3 coatings are widely studied for high temperature solar thermal applications since the coating exhibits high absorptance and low emittance even at higher operating temperatures. The Pt-Al_2O_3 coatings exhibit high thermal stability both in air and vacuum. But the coating is not commercialized due to the high cost of platinum. A large number of solar selective coatings such as Ni-Al_2O_3, Ni-SiO_2, Fe-Al_2O_3, Cr-SiO, Mo-Al_2O_3, Mo-SiO_2, W-Al_2O_3, etc have been developed for high temperature solar thermal applications. But only a few of them such as, Mo-SiO_2, W-Al_2O_3, Mo-Al_2O_3, etc. have been successfully commercialized and are being used in receiver tubes for solar thermal power generation.

In recent years, transition metal nitride based coatings have emerged as novel high temperature solar selective coatings which can be used in solar thermal power plants for electricity generation. Our group has developed a transition metal nitride based solar

selective coating (i.e, TiAlN/TiAlON/Si_3N_4 tandem absorber) for high temperature applications. Recently, Kennedy modeled a solar selective coating with intrinsic solar selectivity and high temperature stability using multiple cermet layers (TiSi-a and TiO_2) along with appropriate surface texturing and incorporating multiple AR coatings (SiO_2). Preliminary results of these coatings are encouraging and further research is currently in progress. Transition metal oxide based solar selective coatings hold great potential in meeting the requirements of high-temperature applications.

In summary, we have carried out an extensive study of the different types of solar collectors for solar water heating and industrial process heating applications. The cermet, multilayer and tandem absorber concepts are widely used to prepare spectrally selective coatings and have been described in this report. We have reviewed the status of sputter deposited solar selective coatings for mid-temperature and high-temperature solar thermal applications. We have also carried out a survey of the commercially available mid and high temperature solar selective coatings. It has to be mentioned that even though a large number of solar selective coatings have been developed by researchers all over the world, only a few of them have been commercialized and are being used for flat-plate/evacuated tube collector and solar thermal power generation applications. The global utilization of the commercially available sputter deposited solar selective coatings has been studied in this report. We have also discussed the current worldwide scenario of parabolic trough plants.

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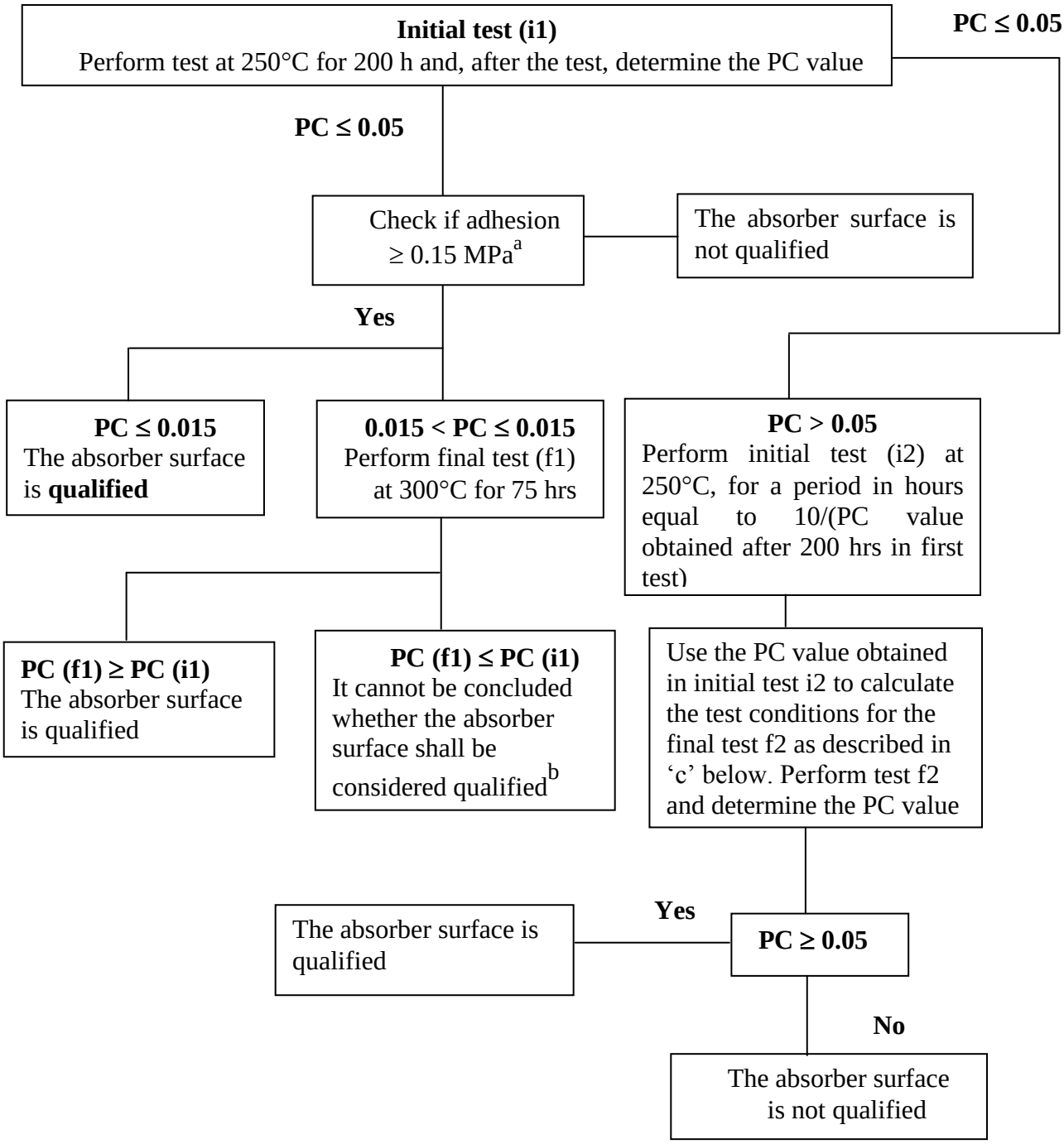
Appendix A: List of some of the major industrial sputtering system manufacturers.

Name of the manufacturer	**System description**
Von Ardenne, Germany*	Vertical and horizontal in-line systems
Kenosistec, Italy**	In-line sputtering system
Vapor Technologies, Inc., USA	Batch system
Hauzer Techno Coating, The Netherlands	Batch system
POLYTEKNIK, Denmark	Roll to roll sputtering system
SVS-Vacuum Coating Technologies, Germany	Linear and cluster inline systems
Best Materials Corporation, Korea	Roll to roll sputtering system
ANATECH, USA	Roll to roll sputtering system
KOLZER, Italy	Batch and in-line sputtering system
CHA Industries, USA	Roll to roll sputtering system
Teer Coatings, UK	Batch and roll to roll sputtering systems
HuiCheng Vacuum Technology Co., Ltd, China	In-line sputtering system
FHR Anlagenbau, Germany	In-line and roll to roll sputtering systems
Applied Materials, USA	Roll to roll sputtering system
KOBELCO Vacuum Web Coater, Japan	Roll to roll sputtering system
Turbosun, China***	Batch system

*Sunselect, TiNOX and IKARUS coatings **ENEA patented coating ***SS-AlN and Al-AlN coatings

Appendix B: ***Testing procedure for qualification of the thermal stability of absorber surfaces.***



Taken from Ref. 35

[a]If a tape test is used to check the adhesion between the coating and the substrate, the adhesion between the tape and the coating should be better than 0.15 MPa.

[b]A more comprehensive investigation of the thermal stability is recommended.

[c]Estimate by interpolation, the testing time, that would correspond to PC=0.05. Determine the lowest acceptable activation energy on the 250°C curve in Fig. 3 from Ref. 35 and also the corresponding failure time in a test at 200°C and perform the test for a period corresponding to that time. Determine after the test PC and if relevant also the adhesion of the coating.

Glossary

Absorptance: The ratio of the radiant or luminous flux absorbed by a body to the flux falling on it. The absorptance of a blackbody is by definition '1'.

Air mass: The ratio of the mass of atmosphere through which beam radiation passes to the mass it would pass through if the sun were at the zenith (i.e., directly overhead).

Antireflection coating: A thin coating of a material, which reduces the light reflection (i.e., front surface reflection) and increases light transmission.

Area concentration ratio: The ratio of the area of aperture to the area of the receiver.

Beam radiation: The solar radiation received from the sun without having been scattered by the atmosphere.

Blackbody: A perfect emitter and absorber of thermal radiation. A blackbody emits radiant energy at each wavelength at the maximum rate possible as a consequence of its temperature and absorbs all incident radiant flux.

Collector: Special kind of heat exchanger used to convert solar energy into thermal energy

Concentrator: It is the part of the collector that directs radiation onto the receiver.

Direct normal radiation: Corresponds to the direct part of the energy carried by sun rays on a given area measured as kWh/m^2 per area.

Diffuse radiation: The solar radiation received from the sun after its direction has been changed by scattering by the atmosphere.

Differential thermopile: When a loop circuit is made of two dissimilar metals and the two junctions between two wires are held at different temperatures, an EMF is produced and a current can be detected with a sensitive galvanometer.

Diffuse reflectance: It is the reflection of light from a surface such that an incident ray is reflected at many angles rather than at just one angle as in the case of specular reflection.

Emittance: A term that describes the ability of a body to emit radiation. It is defined as the ratio of the radiant emission of the body, as a consequence of temperature only, to the corresponding emission of a perfect emitter (blackbody) at the same temperature.

Emissivity: A term reserved for the emittance for the restricted case of an opaque and homogenous material.

Flat plate collector: A solar collection device in which sunlight is converted into heat on a plane surface without the aid reflecting surfaces to concentrate the rays.

Getter: Metallic compounds designed to absorb gas molecules are installed in the vacuum space to absorb hydrogen and other gases that permeate into the vacuum annulus over time.

Hemispherical emittance: Emittance of source averaged over all the radial directions of the overspreading hemisphere.

Infrared radiation: Electromagnetic radiation from the sun that has wavelengths slightly longer than visible light.

Irradiance: The solar power incident on a surface, usually expressed in kilowatts per square meter. Irradiance multiplied by time gives insolation.

Molten salt: Salt mixture which due to chemical characteristics is suitable for thermal storage applications as well as heat transfer fluid (HTF, i.e., liquid mixture of 60% sodium nitrate and 40% potassium nitrate).

Saturated/superheated steam: Saturated steam corresponds to the steam heated at a temperature at which the liquid water and the vapor are in equilibrium. Superheated steam is steam at a temperature higher than water's boiling point. If saturated steam is heated at constant pressure, its temperature will rise, producing superheated steam.

Stirling engine: Heat engine that operates by cyclic compression and expansion of a determined working fluid. There are several types of stirling engines. For STE applications two are used: kinetic and free piston. The main difference between those is the existence of a piston interfacing with the displacer piece.

Normal emittance: Emittance of a source into the direction normal to its surface.

Solar constant: It is the energy from the sun per unit time received on a unit area of surface perpendicular to the direction of propagation of the radiation at mean earth-sun distance outside the atmosphere.

Solar spectrum: The total distribution of electromagnetic radiation emanating from the sun.

Solar thermal electric: Method of producing electricity from solar energy by using focused sunlight to heat a working fluid, which in turn drives a turbo generator.

Spectral emittance: Emittance based on the radiant energy per unit wavelength band.

Specular reflectance: Reflection in a sharply defined direction equal to the angle of incidence from a smooth interface between homogenous materials, i.e., obeying the law of reflection.

Receiver: It is the element of the system where the radiation is absorbed and converted to some other energy form**.**

Thermopile: It is an electronic device that converts thermal energy into electric energy. It is composed of thermocouples connected usually in series or in parallel.

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